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HABILITATION THESIS

TEZĂ de ABILITARE

**NOVEL MATERIALS BASED ON FLY ASH FOR ADVANCED
INDUSTRIAL WASTEWATERS TREATMENT**

**NOI MATERIALE BAZATE PE CENUȘA DE
TERMOCENTRALĂ PENTRU EPURAREA AVANSATĂ A
APELOR UZATE REZULTATE DIN PROCESE
INDUSTRIALE**

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REZUMAT

Lucrarea reprezintă o sinteză concisă asupra rezultatelor obținute în dezvoltarea și modelarea de noi materiale cu proprietăți adsorbante și fotocatalitice, folosite în tratarea avansată a apelor uzate încărcate cu metale și coloranți, utilizând un deșeu - cenușa de termocentrală. S-au studiat și utilizat două tipuri de cenușă obținute din electrofiltrii de la termocentrala (FA) de la CET Brașov și SCE Mintia, cu granulometrie și morfologie diferite. Cenușile cu fracția granulometrică cuprinsă între 20-40 μm (valori care pot influența pozitiv creșterea suprafeței specifice) au fost selectate pentru obținerea materialelor adsorbante.

S-au studiat și s-au comparat proprietățile adsorbante ale FA cu cele ale cenușii obținute la arderea salciei rapid crescătoare.

Compozițiile sunt relativ uniforme, cu predominanța compușilor oxidici. Suma componentelor majoritari (SiO_2 , Al_2O_3 , Fe_2O_3) este în fiecare caz peste 75% și, conform standardelor ASTM, cenușile fac parte din clasa F, adică nu agregă în prezența apei. Compușii solubili (cu precădere oxizii metalelor din gr. I și II) influențează valorile TSD, de conductivitate și de pH, impunând o etapă obligatorie de spălare înainte de utilizare.

Probele de cenușă au fost pretratate cu diferiți reactivi: (1) soluții de NaOH 1N, 2N, 4N; (2) HCl 2N; (3) Complexon III; (4) indicatori: negru eriocrom T și violet de pirocatechina. După 48 h timp de contact, suprafața cenușii se modifică. FA s-a modificat în condiții blânde (temperatura camerei, presiune normală). Cel mai bun agent de modificare s-a dovedit a fi soluția NaOH 2N.

Testele de difracție, analizele spectrale FT-IR, analizele AFM (rugozitate), SEM, determinarea suprafeței specifice, porozității și a energia superficiale confirmă prezența proceselor de dizolvare-reprecipitare, modificând aspectul suprafeței: de la neted (Complexon III, HCl) la fracturat (NaOH 4N), cu consecințe directe asupra eficienței adsorbției.

S-au obținut și analizat materiale compozite din FA cu bentonită și respectiv cu diatomită. Din materialul compozit FA-bentonită s-au obținut peleți care au fost tratați termic la diferite temperaturi și s-a investigat stabilitatea lor în apă. Ca adsorbanti, s-au dovedit eficienți în îndepărtarea albastrului de metilen. După epuizare, acești peleți pot fi refolosiți, de exemplu în obținerea de pavele.

Prezența în compoziția cenușii a diferiților polimorfi de TiO_2 , Fe_2O_3 , MnO_2 poate orienta folosirea acestor cenuși spre obținerea materialelor compozite cu oxizi semiconductori cu bandă interzisă largă, care să producă fotodegradarea poluanților organici în UV și în Vis. S-au obținut și analizat materiale mixte din FA + oxizi semiconductori (TiO_2 și WO_3) folosiți în fotocataliză, în condiții normale de temperatură. Extinzând conceptul, din FA și TiO_2 în condiții hidrotermale ($t = 100^\circ\text{C}$ și $p = 5 \text{ atm}$) s-au obținut noi materiale compozite nanostructurate folosite la îndepărtarea metalelor grele, coloranților și surfactanților prin procese simultane de adsorbție și fotocataliză. Aceste materiale s-au dovedit eficiente în procesul de epurare a apelor uzate provenite din industria textilă.

Utilizând parametrii optimizați (timp de contact, raport masă de cenușă/volum de soluție), s-au studiat și modelat procesele de adsorbție și fotodegradare; descrierea adsorbției cu modelele Langmuir și Freundlich se poate face doar în cazuri limitate, atât la utilizarea soluțiilor mono-ionice cât și a sistemelor poli-cationice de Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} . Eficiența adsorbantului și selectivitatea sa pentru un anumit tip de cation depinde de numărul de hidratare al cationului în condițiile de lucru, de tăria ionică și în special de pH-ul soluției. În sisteme care conțin poluanți organici (coloranți, surfactanți) și metale grele, adsorbția concurentă poate duce la modificarea substratului, prin legarea rapidă a colorantului, cu efect pozitiv asupra reținerii metalelor grele. Sub iradiere procesele sunt inverse: metalele grele se adsorb iar coloranții se fotodegradează, conducând la procese complexe care pot fi controlate pentru eficiențe tehnologic acceptabile. Analizele spectrale, XRD și EDX ale materialelor încărcate cu poluanți după adsorbție/fotodegradare indică noi legături între poluanți și centrii activi de pe suprafața cenușii modificate.

Reacțiile de adsorbție-fotodegradare decurg cu precădere după o pseudo-cinetică de ordinul 2 și de difuzie interparticule.

Amestecuri de FA cu TiO_2 au fost studiate ca pas inițial în epurarea apelor rezultate din industria finisajului textil. Eficiența optimă și viteza maximă de adsorbție s-a găsit pentru un amestec de FA: $\text{TiO}_2 = 3,9:0,1$ g în 100 mL apă.

Materialele obținute prin procedeu hidrotermal în mediu alcalin s-au dovedit a fi mai eficiente, dând posibilitatea reducerii cantității de material adăugat la 100 mL soluție; dezavantajul este separarea mai dificilă a adsorbantului, fiind necesară centrifugarea. De aceea, aceste materiale sunt recomandate în adsorbții statice. Rezultatele obținute se pot aplica în proiectarea unui proces eficient și industrializabil de epurare avansată a apelor uzate, adecvat unui domeniu larg de concentrații de poluanți.

Activitatea de cercetare a condus la rezultate cu grad ridicat de noutate care au fost publicate în jurnale ISI și prezentate în conferințe relevante la nivel internațional și care au fost citate în 98 de articole din jurnale ISI (excluzând autocitățile). Rezultatele s-au obținut în cadrul programului de doctorat, a unui stagiu post-doctoral și printr-un proiect național aflat în derulare. Ele au stat și la baza unei noi propuneri de proiect PNII Parteneriate, aflat în evaluare (94 puncte). Tematica activității de cercetare se reflectă și în activitatea de educație și confirmă capacitatea de a conduce și îndruma grupuri de lucru, inclusiv doctoranzi.

NOVEL MATERIALS BASED ON FLY ASH FOR ADVANCED INDUSTRIAL WASTEWATERS TREATMENT

ABSTRACT

The work represents a synthesis of the results obtained in the development, modelling and optimization of novel materials with adsorbent and photocatalytic properties used in the advanced treatment of wastewaters loaded with heavy metals and dyes, by using a waste - fly ash. There were investigated two types of fly ashes with different grain size distribution and morphology, collected from the electrofilters of the CET Brasov and SCE Mintia power plants (FA). The fly ashes with the grain size between 20-40 μm (values that can positively influence the increase in the specific surface) were selected to obtain absorbent materials.

A comparative study was done on the fly ash and the ash resulted from burning fast growing willow.

The chemical composition of the fly ashes is quite uniform, with a majority oxide content. The sum of the majority compounds (SiO_2 , Al_2O_3 , Fe_2O_3) is for each case higher than 75% thus, according to the ASTM standards, the fly ashes are of F class and do not aggregate in long contact with water. The soluble components, mainly oxides of the group I and II metals, significantly influence the TDS values, the conductivity and the pH, imposing washing fly ash as a compulsory step before use.

To increase the specific surface and the homogeneity, the fly ash samples were conditioned using different reagents: (1) NaOH 1N, 2N and 4N solutions; (2) HCl 2N; (3) Complexone III; (4) indicators: black eriochrome T and pyrocatechol violet. After 48 h contact time, in mild conditions (room temperature, 1 atm.), the fly ash surface is modified. The best conditioning agent was found to be the NaOH 2N solution.

The diffraction and FT-IR data, the AFM (roughness) and SEM analyses, the specific surface, the porosity and surface energy measurements confirm the dissolution-precipitation processes and the modifications in the surface aspect, varying from smooth (Complexone III, HCl) to fractured (NaOH, 4N), with direct consequences on the adsorption efficiencies.

There were obtained and characterised FA-based composites with bentonite and diatomite, respectively. The FA-bentonite composite was further pelletized and annealed/sintered at different temperatures and their water stability was further investigated. As adsorbents, they proved to be efficient in methylene blue removal from aqueous solutions. After exhaust, these pellets can be incorporated in concrete.

Fly ash contains different polymorphs of TiO_2 , Fe_2O_3 , MnO_2 , outlining another possible use in composites, with wide band gap semiconductors, able to photo-degrade the organic pollutants in UV and Vis. Therefore, in a next step there were obtained (at room temperature) mixed materials containing fly ash and semiconductor oxides (TiO_2 and WO_3), recognised as efficient photocatalysts. Extending the concept, novel nanostructured composite materials of FA and TiO_2 were obtained in hydrothermal conditions ($t = 100\text{ }^\circ\text{C}$ and $p = 5\text{ atm}$) and were tested in heavy metals, dyes and surfactants simultaneous removal from wastewaters with complex pollutants load. These materials proved to be efficient in the advanced treatment of wastewaters resulted in textile industry.

Based on the optimised process parameters (contact time, ratio FA mass/solution volume) the adsorption and photodegradation processes were investigated and modelled; the Langmuir and Freundlich isotherms can describe the process on limited domains for the heavy metals adsorption from mono or multi-cation systems containing Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} . The adsorbent efficiency and selectivity for a given cation depend on the hydration number, the adsorption conditions, the ionic strength but mainly on the working pH. In systems that contain organic pollutants (dyes, surfactants) and heavy metals, concurrent adsorption can modify the substrate through the fast binding of the dye, with a positive effect on heavy metals retention. Under irradiation, the processes are reversed: heavy metals are continuously adsorbed and dyes are photodegraded, leading to complex processes that can be controlled for reaching technologically acceptable efficiencies. The spectral analyses, the XRD and EDX data registered on the materials after adsorption/photodegradation outline the development of new bonds between the pollutants and the active sites on the surface of the alkali modified fly ash.

The adsorption-photodegradation processes mainly follow the pseudo-second order and interparticle diffusion kinetics.

The mixtures of fly ash and TiO₂ were studied as an initial step in treating the wastewaters resulted in dyes finishing industry. The optimal efficiency and the highest reaction rate were obtained for a mixture of FA: TiO₂ = 3.9:0.1 g in 100 mL water.

The materials obtained via hydrothermal synthesis in alkali media proved to have higher efficiency, allowing to reduce the corresponding adsorbent amount in 100 mL water; the drawback is the more difficult separation of the adsorbent material, by using centrifugation. Therefore, these materials are recommended for batch processes. The results can be applied in the design of efficient, up-scalable wastewater treatment processes, effective on a broad range of pollutants concentrations.

The research activity allowed obtaining results with a certain novelty that were published in ISI journals and were presented in relevant international events, and which are cited in 98 papers in ISI journals (without self-citations). The results were obtained through the doctoral program, in a post-doctoral project and through a national project under development. They also were the basis of a new project proposal, under the PNII Partnership call (receiving 94 p score), being under evaluation. The research topic is also mirrored in education and confirms the skills required in coordinating R&D groups, including doctoral students.

B. Carrier Path

B.1. Scientific Professional and Academic Achievements

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Abstract

B. Carrier Path

B.1. Scientific Professional and Academic Achievements

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I. Fly Ash - A Second Raw Material for Advanced Wastewater Treatment. State of the Art

I.1. Water - A Valuable Resource

Water is a necessary environmental factor of life, while being an important raw material for the industry, as most chemical reactions occur in aqueous medium. *Saving water to save the planet and to make the future of man kind safe is what we need now.* Most often pollution of surface water is the result of human activity (anthropogenic pollution), with major consequences on the eco-systems and, eventually on the global water resources. The result is now-a days the *water stress* and the forecast is dim if not suitable and concerted actions are planned and implemented all over the world.

Polluted water may be charged with different pollutants, as water is a very good host for multiple substances Fig. 1, depending of the source, for example: the polluted waters from agriculture will contain mostly pesticides, nitrogen fertilizers (phosphate) and salts; sewage water will contain remnants of household (detergents, fats, manure etc.); thermal water are warm and industrial wastewaters contain a broad range of organic and inorganic chemicals.

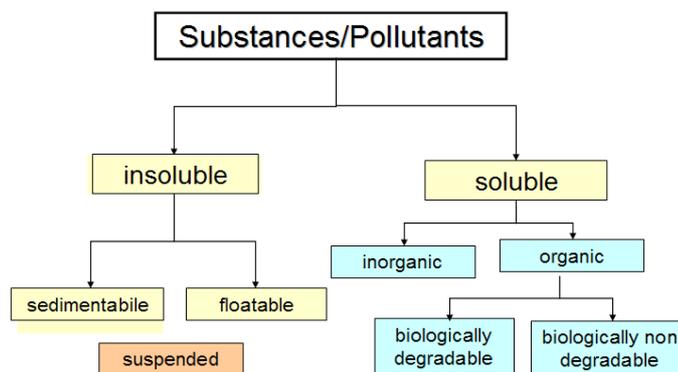


Fig. 1. Classification of the pollutants

Wastewater can be defined as the *water with changed compositions by human and industrial usage which is collected in the sewer main system.*

The sources of water pollutions can be identified as:

- *natural*, caused by natural disasters (floods, storms, volcanic eruptions, earthquakes, fungi, pollen, cosmic dust);
- *anthropogenic (artificial pollution)*, caused by the human activities.

I.2. Industrial Wastewater

The main industries responsible for large amounts of wastewaters, with complex pollutant load are:

a) *The mining and extractive industry* - wastewaters contain large quantities of heavy metals, different organic or inorganic chemical substances. In 2006-2007 the LFS estimated that 18.000 people whose current or most recent job was in this industry suffered from an illness which was caused by the working environment [1].

b) *The chemical industry* - releases wide range of toxic substances:

- petrochemistry (the oilfield industry 82.53 t/yr - BTEX pollutants) [2];
- chlorous soda industry;
- organic dyes industry;
- drugs industry (pharmaceutical);
- fertilizers, pesticides, herbicides, insecticides industry;
- pulp and paper industry.

c) *The light industry*:

- leather industry;
- finishing industry.

d) *The food industry* - the animal and vegetal waste and freon used as refrigerating agents.

e) *The building and construction materials industry* - pollutes the environment with large quantities of powders (CaO, MgO, SiO₂, asbestos).

Energy production also has a significant environmental impact, including on water:

a) *The thermal power plants* - the coal combustion products (CCP) are: fly ash, bottom ash, boiler slag, flue gas desulphurization materials, hot air and water vapors.

b) *The hydro-power plants* - changes the quality of water in the ecosystems.

c) *The nuclear and electrical power plants* - pollute the environment with the high water volumes - for cooling systems and radio-nuclides, gases, liquids and solid materials.

Textile industry followed by the food industry are the largest consumers of water for processing, while the chemical industry uses a large amounts of water for cooling the obtained products and the installations, Fig. 2.

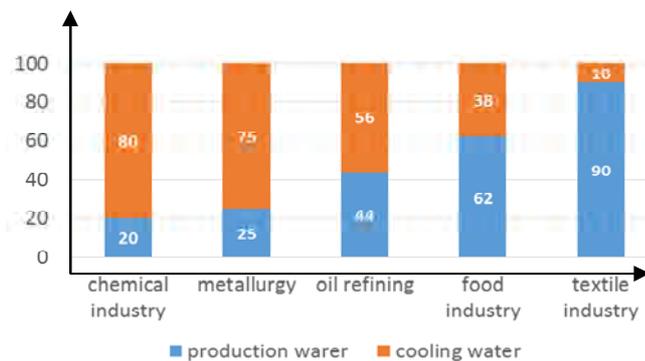


Fig. 2. Distribution of water consumption for different industries [3]

The maritime and air transport generates pollutant resulting from fuel burning (CO, CO₂, NO_x, hydrocarbons (methane, ethane) or from shipwrecks of the oil tank ships (1978 Amoco Cadiz on coasts of Grand British, 1989 shipwreck of the oil tank Prince William Sound near Alaska, 1999 shipwreck Erika near France coast).

Agriculture and animal farming - soil pollution through excessive irrigation, using pesticides herbicides and chemical fertilizers (nitrates and phosphates) which could modify the pH of the soil or the quality of surface and underground waters.

Domestic activities - generate vegetables or animal's fats, detergents agents, biological pollution.

According Nixon et al., 2004 (The use of abstracted water in Europe) [4] the water consumption is presented in Fig. 3, outlining the average industrial consumption of water, except the cooling water.

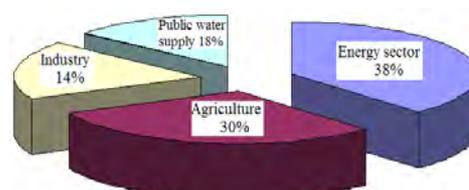


Fig. 3. The use of fresh water in Europe

The nature has its own mechanisms to neutralize the effects of pollutants, but if discharged wastewater flows are high and in too large concentrations the nature can no longer meet this task *because water each has a limited self-purification capacity*. *Water self-purification is natural process involving physical, chemical, biological and bacteriological factors*.

If that limit is exceeded, sudden and irreversible changes may occur in its flora and fauna that might even turn it into dead water (fish dies and become infection sources, both for the natural ecosystem and for public health).

So, water supports life; the water demand is constantly increasing, thus it is a crucial resource for humanity, generating and sustaining the growth economy and for humanity the prosperity that becomes critical. Nearly half the EU population lives in “water-stressed” countries because statistics show that 20% of surface water is at danger risk of pollution; about 60% of the European cities over-exploit their groundwater resources, 50% of wetlands are endangered and huge amounts of water are used in household and in various industrial processes, by far exceeding the self-cleaning limit of nature [5].

The globe’s population will increase at an estimated ten billion in 2050 and less than 1% of the planet’s water is available for human consumption; even now, more than 1.2 billion people all over the world have no access to safe drinking water [Water on Earth, Nixon et al., 2004]. One in 10 people have no access at drinking water and in each year over 700,000 children die from diarrhea caused by dirty water and poor sanitation - that is nearly 2,000 every day [6].

The Water Framework Directive (WFD) is the most important EU directive in the water field and requires “good water status” for European waters by 2015, to be achieved through a system of participatory hydrologic basin management planning and supported by several assessments and extensive monitoring. The framework established by WFD for water management and 13th European Forum on Eco-innovation Action Plan (EcoAP) organised by EC at Lisbon, 2012, declared year 2013 “*United Nations International Year of water cooperation*” and included similar objectives: to prevent further deterioration of the water resources and enhance their status; to promote sustainable water use; to progressively reduce discharges of the priority substances and to phase-out discharges of priority hazardous substances; to progressively reduce groundwater pollution and to contribute to mitigating the effects of floods and droughts.

On the other hand the priority research area of the European Technology Platform for Advanced Engineering Materials and Technologies (EuMaT), set in 2006 a Road-map to be followed up to 2013 and beyond, for implementing radical changes for sustainable development in *modelling, characterization and testing advanced materials and manufacturing, supporting the overall progress of humankind*. These lines are continued in the future research and development program, Horizon 2020.

In this context, the many water pollutants removal must be based on new concepts, technologies and materials. This is especially important in wastewater treatment processes, loaded with a growing variety of pollutants that have adverse environmental effects even at very low concentrations, and therefore need effective and affordable processes based materials and systems new and cheap.

The current trends are to develop low-pollution technologies which can be achieved by developing new technologies based on new materials that produce less waste or less toxic waste through re-use or by integrating natural processes limiting pollution by bioaccumulation.

Special attention is devoted to novel, advanced wastewater treatment processes, aiming at water reuse.

The wastewater treatment processes are a combination of procedures - physical, chemical, biological and bacteriological, designed to reducing the loading of organic, inorganic and bacteriological pollutants in order to protect the environment for obtaining the clean water. The degree of treatment depends on the technologies and the equipment employed to remove a mix of substances (sludge) which in turn must be disposed off, as not to cause any harm to the environment. All this procedures depend on the degree of pollution in the wastewater:

- *dilution ratio - the ratio of the pollutant amount (volume, flow-rate, emission- rate);*
- *the structure of the polluting source (concentrated or dispersed in multiple points);*
- *the type of receptor stream (river, lake, sea, ocean);*
- *the conditions of diffusion and dispersion of the pollutant in the receptor stream;*
- *the nature of the pollutant (physical, chemical (organic, inorganic), biological or bacteriological) the properties;*
- *the form of the pollutant (large or small body, floating matter, miscible or immiscible in water, solid or liquid etc.);*
- *the degree of the persistence, degradability, reaction rate e.g.);*
- *the degree of toxicity of the chemical contaminant.*

The non-biodegradable pollutants involve complex processes, expensive equipment and can be satisfied by employing *advanced methods of treatment (AMT)*. The current trend is to use low cost materials, including wastes, and innovative technologies. The Pollution or toxic effect of a substance depends on its structure and concentration.

The concentration permissible limit (CLA) is the concentration above which a substance may present polluting effect. CLA limits are set depending on the composition of the pollutant, country or group of countries. The admissible discharge values for industrial wastewaters are set at national (and EU) levels and are periodically revised, considering novel findings (e.g. bio-accumulation), thus these limits are constantly lowered. Environment protection Agency in USA (U.S. EPA) proposed a list of 129 compounds grouped into 65 categories, for example: organic compounds, cyanides, asbestos and 13 heavy metals. The Table 1 presents limit values for some pollutants, according the Romanian standard for wastewater discharge sewage networks and treatment plant [7].

Table 1. *Quality indicators of wastewater discharged into the sewerage [7]*

Indicators	Unit	Permissible values
Odor	degrees max.	2
Taste	degrees max.	2
pH	pH units	6.5-8.5
Ammonia nitrogen	mg/L	30
Phenols extractible with water vapours	mg/L, max	30
Suspended matter	mg/L	350
Biochemical Oxygen demand (CBO5)	mgO ₂ /L	300
Chemical Oxygen Demand (CCO)	mgO ₂ /L	500
Aromatic amines	mg/L	0
Total cyanides (CN)	mg/L	1
Substances extractible with organic solvents	mg/L	30
Biodegradable synthetic detergents	mg/L	25
Copper (Cu ²⁺)	mg/L	0.2
Zinc (Zn ²⁺)	mg/L	1
Lead (Pb ²⁺)	mg/L	0.5
Cadmium (Cd ²⁺)	mg/L	0.3
Total chromium (Cr ³⁺ + Cr ⁶⁺)	mg/L	1.5
Hexavalent chromium (Cr ⁶⁺)	mg/L	0.2
Free residual chlorine (Cl ₂)	mg/L	0.5
Sulfides and hydrogen sulfide (S ²⁻)	mg/L	1
Sulfites (SO ₃ ²⁻)	mg/L	2
Sulfates (SO ₄ ²⁻)	mg/L	600

I.3. Methods for Pollutants Removal from Wastewaters with a Complex Load

The main dangerous pollutants in wastewater resulted from metal finishing, dyes manufacturing and textile industry and food processing are:

- heavy metals;
- dyes;
- surfactants.

I.3.1. Heavy Metals in Wastewaters

The term heavy metal (HM) refers to 20 metals that have a relatively high density (above 5 g/cm³) and are toxic or poisonous at low concentrations, for example: cadmium, chromium, mercury, lead, copper, nickel, zinc, iron, e.g.

The main sources of heavy metals in wastewater and surface water are various industries [8]:

- electroplating and metal surface treatment processes;
- metallurgy, metal and plastics coating;
- metallurgy of easily fusible alloys;
- electrotechnic industry and rechargeable batteries manufacturing (Ni-Cd);
- electronic industry;
- paint manufacture; inorganic pigments, dye finishing;
- leather industry;
- oil refining;
- mining.

The largest amount of heavy metals (t/yr) from industry are discharged directly into rivers; in Europe, in 2001 huge amounts of HM were discharged: 864 t/yr chromium, 71.5 t/yr nickel, 45.8 t/yr copper, 41.7 t/year lead, 8.1 t/year cadmium, 5.1 t/yr arsenic and 0.5 t/yr mercury [8], as Table 2 [9] shows.

Table 2. *The releases of the main pollutants released directly into water from the industrial sector in Europe 2001*

Compound	t/yr.	Main source
Phenol	1419,34	Basic inorganic chemicals or fertilizers (47%)
Total organic carbon	246,52	Industrial plants for pulp from timber or other fibrous materials, and paper or board production (70%)
Nitrogen	22,317	Basic inorganic chemicals or fertilizers (29%)
Phosphorus	1662	Basic inorganic chemicals or fertilizers (25%)
Chromium	864	Metal industry (87%)
BTEX	82.5	Basic organic chemicals (56.1%)
Nickel	71.5	Metal industry (45%)
Copper	45.8	Metal industry (23%)
Lead	41.8	Metal industry (40%)
Cadmium	8.1	Metal industry (66%)
Arsenic	5.1	Metal industry (22%)
Mercury	0.5	Metal industry (23%)
Polycyclic aromatic hydrocarbon	10.3	Metal industry (74%)

Heavy metals are persistent pollutants, non-biodegradable and can be accumulated easily in organisms even at low concentrations, causing serious illness; common effects on humans are described as: increased salivation, severe stomach irritations leading to vomiting and diarrhea, abdominal pain, choking, high blood pressure, iron-poor blood, liver disease, pancreas and nerve or brain damage, poisoning by ingestion include vomiting, vomiting of blood, hypotension, coma, jaundice, and gastrointestinal pain [4]. For avoiding flora, fauna and health problems, the discharge limits are strict and require advanced wastewater treatment processes [10].

In water the heavy metals cations are hydrated with different bipolar water molecules Fig. 4.

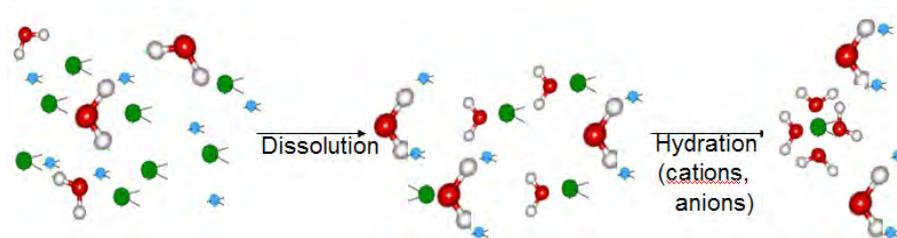


Fig. 4. *Water interaction with heavy metal cations and anions*

The hydrated ions are more toxic than the metal atoms, are faster absorbed and disturb the enzymatic processes.

I.3.2. Dyes in Wastewaters

The main sources for these wastewaters are: textile and plastic industry, leather, cosmetic, pharmaceutical, food preparation dyes and paints manufacturing.

There are over 10.000 commercial dyes available today and yearly there are produced 7×10^5 tons of dyes [11] with complex chemical structure (with aromatic rings); on average 2% of these are exhausted in aqueous effluents, while 10% of dyes are lost during the dyeing process [12] and remain in the environment for a long time. The main indicator of water pollution is color, which in addition to unsightly problem (even at concentration below 0.005 mg/L) also brings other problems such as inhibition of photosynthesis because many dyes are toxic and eutrophication thus affecting aquatic organisms; many dyes are carcinogenic, mutagenic and can harm the kidneys, the liver, reproductive system, brain and central nervous system [13, 14].

Supplementary, colour removal does not necessarily end up with complete de-pollution (mineralization), some of them turn into toxic by-products more harmful (un-saturated hydrocarbons, carbonyl and carboxyl products etc.) [15, 16] because have a high chemical stability to light and oxidation and are hardly biodegradable.

Wastewaters resulted in the dye finishing industry have high BOD to COD values ($> 2,000 \text{ mg O}_2\text{L}^{-1}$) while the discharge limits [17, 18] are much lower ($\text{BOD} < 40 \text{ mg O}_2\text{L}^{-1}$; $\text{COD} < 120 \text{ mg O}_2\text{L}^{-1}$), indicating the need for wastewater treatment, because most of the dyes are slowly or non-biodegradable.

Most of the wastewaters resulted in the dye finishing industry are also containing additives (solubility and anti-foaming agents, pH conditioners, whitening agents etc.) and heavy metals, making the wastewater treatment complex and difficult. Toxicological studies show that the most bio-toxic heavy metal is cadmium (also part of some metal-complex dyes), while dyes and pigments are affecting water transparency, reducing light penetration and gas solubility in water [18], also being mutagenic to human.

Some of them turn into toxic by-products [19, 20] because they have a high chemical stability to light and oxidation and are hardly biodegradable.

I.3.3. Methods for Pollutants Removal

There are many physical, chemical and physical-chemical methods to remove pollutants. As heavy metals and dyes impose significant environmental threats, the main removal methods are further outlined.

I.3.3.1. Heavy Metals

Removal of heavy metals in high concentration in wastewater requires two steps:

1a. *Chemical precipitation* - adding reagents to form low-soluble heavy metals compounds (hydroxides, sulfides, carbonates). Low soluble compounds are dissociated in very low proportion (being characterized by the solubility product, P_s), thus dissolved heavy metals remain in water in small amounts, usually higher than the discharge limits.

1b. *Coagulation and flocculation* - adding gelling reagents: $Al_2(SO_4)_3$, $Al_2(SO_4)_3$ with $Ca(OH)_2$, $AlCl_3$, $NaAlO_2$ or $FeCl_3$ or $Fe_2(SO_4)_3$ with/without the addition of $Ca(OH)_2$, $FePO_4$, $Fe_3(PO_4)_2$, tricalcium fosfat - $Ca_3(PO_4)_2$.

Usually the remnant value is over the CLA and advances treatment processes are compulsory.

2. Depending on the initial composition, many alternatives for advanced wastewater treatment are proposed:

- adsorption: regular adsorption, ion exchange adsorption processes [21, 22]; reaction of complexing followed by adsorption of the metal complex on a substrate [23].
- reduction reactions and electrochemical processes [24];
- removal by evaporation;
- membrane processes: microfiltration (MF); ultrafiltration (UF) [25]; nanofiltration (NF) [26]; electrodialysis (ED); reverse osmosis [27].

Choosing one or more complex solutions is subject of efficiency and cost analysis reported at large quantity of wastewater. Among these, adsorption technologies have several advantages: *easy operation and well known technology, inexpensive equipment, less sludge, adsorbents' reuse after desorption.*

I.3.3.2. Dyes

Wastewater containing dyes are hard to treat because the organic molecules are persistent to aerobic digestion and are designed to have good resistance to light. Synthetic dyes cannot be easily and efficiently removed from wastewater by traditional methods at affordable costs. The methods of dyes removal can be divided in three classes: biological [16, 28, 29], chemical and physical [28, 30] methods and are presented in Table 3.

Table 3. *Methods for dyes removal from wastewater*

Biological Methods	Chemical Methods	Physical Methods
<ul style="list-style-type: none"> - Bleaching in the presence of fungicides; - Adsorption on microbial biomass; - Aerobic and anaerobic degradation; - Bioremediation; - Nitrification, denitrification; - Fermentation reactors; - Activated sludge tanks. 	<p><i>Oxidative processes</i></p> <ul style="list-style-type: none"> - photochemical oxidation (Fenton reactions); - heterogeneous photo-catalysis; - ozonation; - oxidation with NaOCl; - electrochemical oxidation; <p><i>Coagulation</i></p> <p><i>Flocculation combined with flotation</i></p> <p><i>Precipitation-Flocculation with Fe(II)/Ca(OH)₂</i></p> <p><i>Electrocoagulation</i></p> <p><i>Ion exchange</i></p>	<ul style="list-style-type: none"> - Physical Adsorption - Irradiation - Membrane processes (microfiltration, ultrafiltration, nano-filtration, reverse osmoses)

These methods have advantages and disadvantages, depending on the load in wastewaters. In Table 4 there are summarized several advantages and disadvantages of the methods for dyes removal.

Table 4. Advantages and disadvantages of removal methods for dyes from wastewater [19]

No.	Method	Advantages	Disadvantages
1.	Bleaching in the presence of fungicides	- high bleaching of anthraquinone and indigoid dyes	- low rate of azo dyes bleaching - requires a bioreactor and an external source of carbon - requires acidic pH (4.5-5)
2.	Fenton reagent	- effective bleaching of soluble and insoluble dyes	- sludge generation
3.	Ozonation	- gases are applied, no alteration of the volume	- small half-life (20 minutes)
4.	Oxidation with NaOCl	- initiates and accelerates the breaking of azo bonds	- aromatic amines release
5.	Photochemical oxidation	- doesn't generate sludge	- by-products formation
6.	Coagulation-Flocculation	- removal of insoluble dyes - economically feasible - simple	- sludge generation
7.	Ion exchange	- regeneration possibility, the adsorbent is not lost	- not effective for all types of dyes
8.	Adsorption	- <i>activated carbon is among the best adsorbents</i> - <i>reduced quantity of organic substances and particulate matter</i>	- <i>high costs of activated carbon</i>
9.	Irradiation	- effective at laboratory scale	- requires a large amount of dissolved O ₂
10.	Micro-ultrafiltration	- low pressure needed	- low quality of treated water
11.	Nano-filtration	- separation of low molecular weight organic compounds and of divalent ions derived from monovalent salts - wastewater treatment of waters with high concentrations of dyes	- high operation costs
12.	Reverse osmosis	- removal of mineral salts, dyes and chemical reagents	- high pressure needed

I.4. Adsorption. Adsorption Mechanisms

Many phenomena which we now associate with adsorption were known from antiquity. The ancient Egyptians, Greeks and Romans used materials as clays, sand and wood charcoal to make the vessels for preserving drinking water [26].

The term of adsorption is universal and means: enrichments of one or more of the components in the region between two bulk phases (the interfacial layer). Adsorption is present in many natural, physical, biological, and chemical systems, and is widely used in industrial applications. The applications of adsorption are well established as means of separating mixtures into two or more streams, each enriched in a valuable component. In this context one of these phases is a solid (and seldom a liquid) and the other one is a fluid (gas or liquid).

The adsorption process is accompanied by absorption - the penetration of the fluid or gas *into* the solid phase.

The participating phases in adsorption are:

- the *adsorbate*: gas (G), liquid (L₁), solid (S)
- the *adsorbent (substrate)*: usually a solid (S) or a liquid (L).

Usually adsorption processes can be described as adsorbate/adsorbent: G/L₂; G/S; L₁/L₂; L₁/S.

The terms *adsorption* and *desorption* are often used to indicate the direction from which the equilibrium states have been approached. Adsorption hysteresis arises when the amount of adsorbent is not brought to the same level by the adsorption and desorption approach to a given equilibrium pressure or bulk concentration. The correlation equation at constant temperature, between the amounts absorbed and the equilibrium pressure or concentration is known as the *adsorption isotherm*.

Adsorption is a physical-chemical process and consists in interactions between the substrate and the molecules in the fluid phase. Two kinds of forces are involved, which give the type of adsorption:

- *physisorption* - adsorption without chemical bounding;
- *chemisorption* - adsorption involving chemical bonding.

The physisorption forces are the same as responsible for condensation, while the chemisorption interactions are essentially being responsible for the formation of chemical compounds. Some important features which distinguish physical adsorption chemisorption are summarized in the Table 5 [31].

Table 5. *Physical adsorption and chemisorption comparison*

Chemisorption	Physisorption (van der Waals)
<ul style="list-style-type: none"> - Chemisorption is dependent on the reactivity of the adsorbent and adsorbate. - Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to only a monolayer. - Chemisorbed molecules lose their identity (result is a new chemical compound) and cannot be recovered after desorption. Electron transfer leading to bond formation between sorbate and surface. - Variation in chemisorption energy is comparable in magnitude to the energy in a chemical reaction. - <u>Adsorption enthalpy</u> wide range, related to the chemical bond- strength E [80-600]KJ/mol, Fig. 5. - Activation energy is often involved in chemisorption and at low temperature the system may not have sufficient thermal energy to attain thermodynamic equilibrium. - Often is an activated process that may be slow and irreversible. 	<ul style="list-style-type: none"> - The physisorption is a phenomena with low degree of interaction. - At high relative pressures physisorption generally occurs as a multilayer. - In physisorption the molecules keep their identity and in desorption in liquid they maintain their the original structure. - Bipolar interaction, without electron transfer leading to bond formation between sorbate molecules and the surface of the adsorbent. - Physisorption is always exothermic, but the energy involved not much larger than the energy of condensation of the adsorbate, typically E [5-40] KJ/mol, Fig. 5. - Physisorption systems generally reach fast equilibrium; equilibrium may be slowly reached if the transport process is rate-determining.
<ul style="list-style-type: none"> - <u>Kinetics of adsorption</u> - highly variable. - $V_{ads.} = V_{des.}$ at equilibrium. - Hard desorption - can be irreversible. - The adsorbent reuse is difficult or impossible. 	<ul style="list-style-type: none"> - Fast kinetic, because it is a non-activated process and reversible; - Easy desorption, the process can be reversible; - The adsorbent can be very easily reused.

Adsorption \longleftrightarrow Desorption

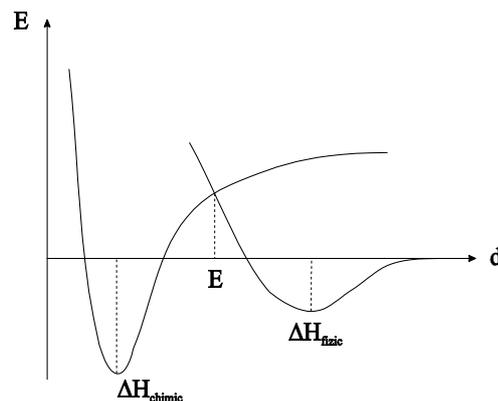


Fig. 5. *Energy variation during adsorption*

The adsorption mechanism depends on the bonds that are formed, the nature of solution (electrolyte or non-electrolyte) and the adsorbent system (crystalline or amorphous).

The type of bonds between the sorbate and the substrate can be: Van der Waals, dipole-dipole, ionic or covalent and depend on the adsorbed molecule (non-polar, polar), or ion and the type of substrate.

The adsorption coefficient depends on two thermodynamic parameters: temperature (T) and pressure (p) for gases or vapors, and temperature and concentration (c) for adsorption from solutions. These parameters (Γ , T, p or c) are related by the functional relationship expressed by the general thermodynamic Eq. [32]:

$$f(\Gamma, T, C) = 0 \quad \text{or} \quad f(\Gamma, T, p) = 0, \quad (1)$$

$$f = \Gamma(T, c) \quad \text{and} \quad \Gamma = f(T, P), \quad (2)$$

where:

$$\Gamma = \frac{n_{\text{sorbite}}}{m_{\text{adsorbent}}} \text{ [mol/g]}. \quad (3)$$

At constant temperature and in solutions this equation is known as Adsorption isotherm $\Gamma = f(c)$.

The shape of the graphical representation of this equation is specific for each adsorption mechanisms, therefore the adsorption isotherms are powerful tools in investigating and optimizing the adsorption processes.

Most of the technologically important adsorption from solutions is exceedingly complex and most of the experimental dates reported in literature were obtained for adsorption processes investigated in relatively dilute binary solutions.

Langmuir Isotherm - the simplest theoretical model was originally developed based on the concept of monolayer adsorption (Nobel Prize in chemistry 1932) to represent chemisorption on a set of distinct localized adsorption sites.

The basic assumptions on which the model is based are:

- molecules are adsorbed on a fixed number of well-defined localized sites;
- each site can hold one adsorbed molecule;

- all sites are energetically equivalent;
- there is no interaction between molecules adsorbed on neighboring sites.

The model leads to the following Eq. [33, 34, 35]:

$$\Gamma = \Gamma_{\max} \frac{ac}{1 + ac} \quad (4)$$

The linear form is:

$$\frac{c}{\Gamma} = \frac{1}{\Gamma_{\max} a} + \frac{c}{\Gamma_{\max}} \quad (5)$$

The Langmuir parameters are:

$$a = \exp(\Delta H_{ads}/RT) \quad (6)$$

and Γ_{\max} , the maximum adsorption coefficient, calculated when all the active sites are hosting an adsorbed molecule.

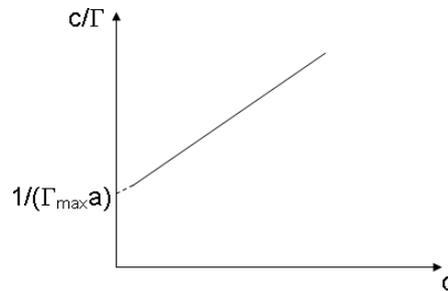


Fig. 6. Langmuir isotherm $\Gamma = f(c_{ads})$

The equation can be re-written using the mass adsorption coefficient. For a given adsorbate, I, the mass adsorption coefficient is usually denoted with “q” and the equation is:

$$q_i = q_{i,\max} \frac{a \cdot c_{i,e}}{1 + a \cdot c_{i,e}}, \quad (7) \quad \frac{c_{i,e}}{q_i} = \frac{1}{q_{i,\max} \cdot a} + \frac{c_{i,e}}{q_{i,\max}} \quad (8)$$

Another very much used adsorption equation is the **Freundlich Isotherm**, an empiric equation that well describes the process on heterogeneous substrates:

$$q_i = k_f \cdot c_{i,e}^{1/n}, \quad (9)$$

where: k_f is Freundlich constant, an indicator of the adsorption capacity, and the $1/n$ dimensionless parameter is a measure of the adsorption density.

The linear form is:

$$\ln q_i = \ln k_f + \frac{1}{n} \ln c_{i,e}, \quad (10)$$

where: k and n - the Freundlich parameters.

The efficiency of the adsorbent materials can be characterized by:

$$\eta_i = \frac{(c_i - c_e)}{c_i} \cdot 100. \quad (11)$$

I.5. Materials Used As Adsorbents. Low Cost Adsorbents

There are a number of different factors which may affect the level of uptake and the adsorption energy from solutions:

The *chemical structure* and *electrical properties* of the solid surface:

- *no polar network (atomic) pure graphite, activated carbon;*
- *polar (ionic network) SiO_2 , TiO_2 , silicates, aluminosilicates;*
- *amphoteric: wool, silk, amphoteric membranes (bipolar);*
- *negatively charged surface (acidic adsorbent, many natural ceramics) - can adsorb cations;*
- *positively charged surface (alkaline adsorbent) - can adsorb anions.*

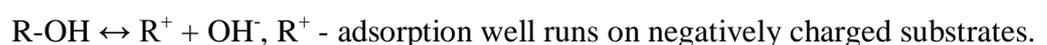
It is to note that by pH control the surface charge of the adsorbent can be modified.

Considering electrostatic interactions, the types of ions and the surface charge should be well matched, to promote efficient adsorption. One example is the dyes:

- acid dyes:



- basic dyes:



Further on, the substrate should have:

- large specific surface area;
- high selectivity;
- high adsorption rate;
- high desorption rate;
- low residual retention of the substance adsorbed - hysteresis null;
- mechanical and thermal resistance.

Other factors affecting the adsorption process are:

- the molecular/micelle polymeric structure of the solution;
- the ionic strength and type of ions;
- the concentration of the adsorbed specie(s) in the solution.

The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they present a large surface area per unit weight. Activated carbon was a most widely used of all the general-purpose industrial adsorbents. They are manufactured from a variety of precursors, cheap and available materials such as wood, peat, coal, coconut shell [36], bark of eucalypt [37] and bones. It is produced by roasting organic material to decompose to granules of carbon. The surface area is over 200 m²/g. Super-active carbons are now made on a commercial scale with BET areas of 3000 m²/g. In 1995, the world annual production of activated carbon was estimated to be in the region of 400 000 tones with increasing consumption at about 7% per annual [38].

Silica gel is a matrix of hydrated silicon dioxide. The properties of typical silica gels are presented in Table 6 [39].

Table 6. *The properties of typical silica gels*

Gel type	Porosity	BET [m² · g⁻¹]
Aerogel	Macro	800
G-Xerogel	Meso	350
S-Xerogel	Meso	500
	Micro	700

Alumina is mined or precipitated aluminum oxide and hydroxide. Although activated carbon is better adsorbent material for adsorption, its black color persists but is very expensive.

However to develop an adsorption process at industrial and commercial scale requires the availability of a suitable adsorbent in tonnage quantities at feasible cost. This has stimulated fundamental researcher in adsorption and led to the development of new adsorbents. A large application of adsorption as a separation process was greatly enhanced by the development of molecular sieves adsorbents and especially the synthetic zeolites.

Low cost adsorbents

Although highly performant, zeolites are quite costly. Therefore many studies are recently focusing on low-cost, highly efficient adsorbents. The low cost adsorbent materials can be:

- *natural compounds*: clays, bentonite [40] with SiO₂ content above 60%, diatomite pillared layer [41] kaolinite, smectites, vermiculites, palygorskites;
- *volcanic tuff, zeolites* [42], *cellulose, chitin* [43];
- *red mud - resulted from the aluminum processing* [44];
- *agricultural by-products* [45] have been tested for removal heavy metals and colors from wastewater such as: apple, pomace [46], wheat straw, wheat bran, coir pith [47] corncobs or barley husks [48], rice husk [49], peanut hulls [50], orange peel [51, 52], different type of sawdust [53], powder of different leaves [54, 55, 56];
- organic artificial or synthetic waste - *bone char* [57], *scrap rubber, humus, or bituminous coal* [58];
- *wood based biosorbents*: *wood sawdust (raw), pine sawdust* [59], *maple sawdust* [60], *cedar sawdust* [61], *straw, seeds hulls* [62], *wheat bran, sawdust oak* [63], *wood fiber* [64], *treated cotton* [65, 66].

The use of materials with high content of cellulose and lignin [43] both in agriculture and forestry is based on their capacity due to the alcohol groups, to adsorb pollutants from wastewater by ion exchange or electrostatic forces.

- *Peat* [67], *sugar beet pulp* [68], *marine alga Padina* [69] or, *activated sewage sludge* [70, 71, 72];
- *Chitosan* - obtained from chitin (natural biopolymer) - found in shell fish. Chitosan is a good adsorbent for all heavy metals and low cost [73, 74, 75].

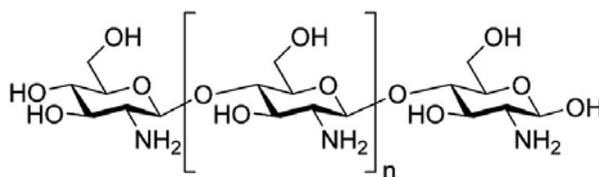


Fig. 7. Structure of chitosan

The tungsten from ground water or may exist due to mining activity, can be removed using a biosorbent “chitosan coated montmorillonite clay”. Clay minerals are a phyllosilicates (sheet like structure) made up of silicate tetrahedron rings which are linked by shared oxygen to other rings in a two dimensional structure. Clay minerals are into four groups: kaolinite, montmorillonite/smectite, illite and chlorite [76]. The clay is widely used because of their high specific surface area, chemical and mechanical stability, structural properties and low cost. The price of clay is about 0.005-0.46/Kg which is 20 times cheaper than activated carbon. Coating clay particles with chitosan shifts the net surface charge of clay from negative to positive and the point of zero charge (PZC) of clay from 2.8 and 5.8 [77].

Clay has a capability to adsorb the metal cations (such as Zn^{2+} , Pb^{2+} , Cd^{2+} and Cu^{2+}), because of the negative charge on the surface but the clay minerals are a little or no affinity for anionic species such as WO_4^{2-} . Therefore the clay minerals surface should be modified to incorporate positively charges sites prior to any anion adsorption attempts. The adsorption isotherms for both biosorbent and natural clay were found to be Langmuir model. The mechanism of tungsten adsorption is pH dependent, being highest at pH 4.

- *Peat moss* - a complex soil materials containing lignin and cellulose, with large surface area ($>200\text{ m}^2/\text{g}$), highly porous [78]. The price of 0.023 dollar/Kg.
- *Ash: wood ash* [79] or *fly ash from power plants using coal* [80].

Ash, resulting from burning coal or biomass is a mixture of oxides with unburned carbon and other minority inorganic compounds thus has a predominant negative surface charge and represents a promising adsorbent.

Recent times, it investigates the removal of dyes from industrial wastewaters by adsorption on the different materials considered as waste.

Many researchers from different countries (Spain, Italy, Greece, China, Africa) were tested the fly ash in adsorption of methyl orange, methylene blue [80, 81, 82, 83].

Many applications in wastewater treatment are already reported, most of them at pilot scale. The use of wood ash is mostly reported for heavy metals adsorption [78, 84] and also for industrial wastewater resulted from dyes manufacturing and textile industry [85, 86]. Experiments using methylene blue as testing dye are reported on rice husk ash [49, 87] and other ash types, being explained by the significant amount of unburned carbon [88, 89].

Fly ash, the lightest fraction resulted in coal burning is also largely investigated for heavy metals and dyes adsorption [88, 90] because the priority compounds from fly ash favours the heavy metals adsorption and are active sites in dyes' immobilization.

For fulfilling the industrial requirements, low-cost adsorbents are intensively studied, mainly based on natural compounds or on wastes.

Heavy metals (cadmium, cooper, zinc, nickel, lead, iron) removal was reported on red mud [91], natural zeolite [41], wood based biosorbents [92], wood sawdust (raw) [93], pine sawdust [94], sawdust cherry, sawdust oak [95], treated cotton [66] scrap rubber, bituminous coal, peat [58], sugar beet pulp [68], marine alga *Padina* [69], microalgae, bacteria [96], fungi, crab shells [97, 98], eggshells [99] or bone char [57].

Other no conventional sorbents from agriculture have been tested for removal heavy metals and colours from wastewater such as: apple, waste pomace of olive oil factory [100], wheat straw, wheat bran [69], coir pith, corncobs or barley husks [47], peanut hulls, orange peel, and different type of sawdust [81], powder of different leaves.

Many studies are reporting on fly ash tested as adsorbent for heavy metals removal and a large amount of fly ash was tested that adsorbent for removal of heavy metals from wastewater [101, 102, 103, 104].

More and more are now investigated the optimized fly ash compositions to obtain an efficient adsorbent able to remov heavy metals and dyes from wastewaters with complex composition.

Ash, resulting from burning coal or biomass is a mixture of oxides with unburned carbon and other minority inorganic compounds thus has a predominant negative surface charge and represents a promising adsorbent.

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I.6. Photocatalysis

Traditional treatment technologies based on activated carbon adsorption is successfully used to remove organic matter (dyes, COV, surfactants) from the water, but its regeneration (by thermal desorption) is expensive and generates other environmental problems.

An alternative to conventional water treatment processes are advances oxidation processes (AOP), defined as processes that occur at normal temperature conditions involving the generation of highly reactive species (the hydroxyl radical) in an amount sufficient to be effective in water purification processes [107, 108].

The (AOP) are characterized by a radical mechanism initiated by free radicals or by interaction of photons with the molecules or chemical species present in solution or with a catalyst. Advanced oxidation methods may be used alone or in combination with conventional treatment methods.

Advanced oxidation processes are:

1. *Photolysis UV* - under the influence of UV radiation the chemical bonding from organic pollutants breaks, resulting various byproducts of photolysis. By photolysis of water with UV radiation are obtained HO• radicals according to Equation 12, which react with any organic pollutant destroying:



2. H_2O_2 in combination with UV radiation and Fe^{2+}/Fe^{3+} , to improve the efficiency of pollutants degradation:

a) H_2O_2/UV ;

b) Fenton $H_2O_2/Fe^{2+}/Fe^{3+}$.

The reactivity of the system $H_2O_2/Fe^{2+}/Fe^{3+}$ was discovered by H.J.H. Fenton and the mechanism Haber-Weis revealed that the hydroxyl radical acts as oxidant in the Fenton reaction:



where: M is a transition metal Fe or Cu.

c) Photo-Fenton UV/ H_2O_2 /Fe (II)

With UV radiation the Fe(II) used in reaction (13) is regenerated and produces an additional quantity of hydroxyl radicals (14):



Due to the high concentration of $HO\bullet$ the UV/ H_2O_2 /Fe(II) system provides a high oxidation rate of pollutants in wastewater compared with advanced oxidation processes (AOP).

The reaction rate also depends on:

- the amount of Fe^{2+} ;
- the amount of H_2O_2 ;
- the pH should be kept in the range of 3-5, if the pH increases iron precipitates as $Fe(OH)_3$ and decomposes the H_2O_2 [109].

In photocatalysis, H_2O_2 acts both as electron acceptor (reducing recombination) and as a hydroxyl radicals' source.

The interaction of the UV radiation with the oxidizing agent depends on the wavelength as the hydrogen peroxide absorbs UV radiation with $\lambda = 200$ nm radiation.

The main disadvantages of homogeneous (photo) catalytic AOPs are related to the costs of chemicals and to the lack of complete control on the end-products.

Heterogeneous photocatalysis AOP (two active phases - solid and liquid) are highly investigated over the world and represents a technology based on a catalyst irradiation; the

photocatalysts are usually semiconductors, which can be photo-excited forming charged pairs of electron-donor and electron-acceptor. A broad variety of materials are reported as efficient photocatalysts, mainly as wide band gap semiconductors.

The best and most cited photocatalyst is TiO_2 , particularly Degussa P25 nano-powder [110] (25% rutile and 75% anatase) which is usually mentioned as reference. Titanium oxide is usually chosen because of its properties: *biologically and chemically inert, stable at chemical and photochemical corrosion, inexpensive. Titania (as anatase or rutile polymorphs) absorb at $\lambda = 387 \text{ nm}$, thus under solar irradiation only the UV part of the spectrum can be used* [111]. Other options are the, WO_3 , ZnO , SnO_2 [112, 113].

Heterogeneous photocatalysis relies on the generation of electron-hole pairs when a photon of energy higher or equal to the band gap energy of the semiconducting photocatalyst (E_g) is absorbed. The electron-hole recombination on the surface or in the particle bulk represents the mechanisms that deactivates the photocatalyst, while their trapping in surface states leads to reactions with chemisorbed O_2 and/or $\text{OH}^-/\text{H}_2\text{O}$ molecules to generate reactive species, such as $\text{O}_2^{\bullet-}$, HO_2^{\bullet} and OH^{\bullet} radicals, which will further oxidise the organic pollutants, Fig. 8 [114].

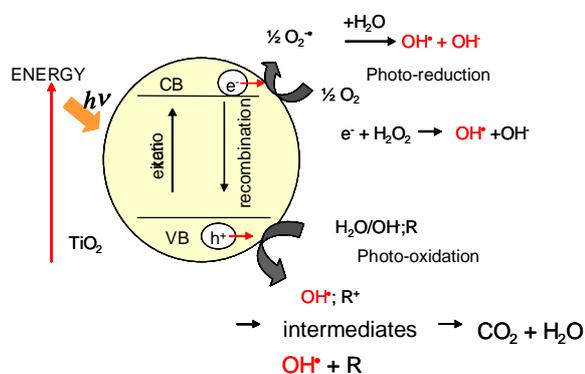
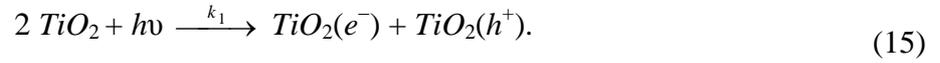


Fig. 8. Heterogeneous photocatalytic process

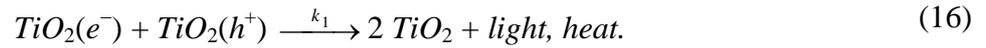
The photocatalyst efficiency varies with the amount of material, with the specific surface, the light intensity and wavelength profile (spectrum). The target of the (AOP) is the pollutants mineralization, the step-by-step decomposition of the organic pollutant molecules on the surface of the photocatalyst until all the pollutant and organic by products are oxidized to CO_2 and H_2O .

The most important processes in the heterogeneous photocatalysis are [114]:

1. Charge carriers generation: electrons (e^-) in the conduction band and holes (h^+) in the valence band:



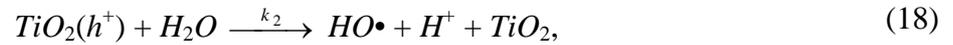
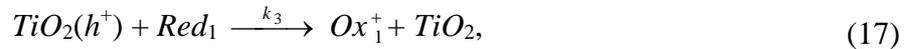
2. Electron-hole recombination:



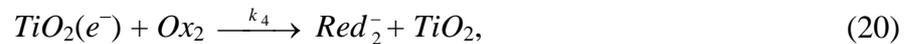
This reaction is responsible for the rather low efficiencies of the photocatalytic processes and imposes the use of wide band gap semiconductors.

3. Reaction on the surface:

3.1. The positive holes are strong oxidants and oxidized or directly react with the electron donor groups from the compounds in the system (e.g. water or hydroxyl ions), to form hydroxyl radicals:



3.2. The photogenerated electrons can react with oxygen forming the superoxide radicals ($\text{O}_2^{\bullet-}$), that further act as oxidants in the reaction with neutral molecules, radicals and ions formed at the surface of catalyst:



4. Degradation

The radicals and ions formed at the semiconductor surface can be involved in the following processes:

- Chemical reaction with compounds adsorbed on the surface of the semiconductor (compounds degradation);
- Recombination in reactions with electron transfer (deactivation);
- Diffusion from the semiconductor surface participating in chemical reactions in solution.

Recent studies outlined the significant influence of dye structure on the degradation efficiency: the anionic dyes are degradable in higher proportion under acidic pH ($\text{pH} < \text{pH}_{\text{pzc}}$) and the cationic dyes are degradable at $\text{pH} > \text{pH}_{\text{pzc}}$. At low pH values the majority species are considered to be the holes while the hydroxyl radicals are the predominant species at higher values of pH or equal to 7:



In other words, in an alkaline media these kinds of species come from the phenomenon described above as well as by their generation on the surface of the catalyst, so a higher efficiency is expected in an alkaline or neutral media.

Alkaline values of pH can be favorable in case of anionic azodyes photodegradation, limiting their adsorption on the negative surface of the catalyst. In acidic media, the TiO_2 molecules tend to agglomerate (to cluster), and this leads to the reduction of the available surface area for the adsorption of photons or dye molecules. Still, as in efficient photocatalysis the first step is the adsorption of the species of interest (dye, organic pollutant etc.), actually a limited pH window is suitable both for adsorption and for generating the photocatalytic species:

pH	pH_{pzc} (catalyst)			pH_{pzc} (dye)				
Surface charge of the catalyst	+	+	0	-	-	-	-	-
Dye charge	+	+	+	+	+	0	-	-

Thus, the recommended range is between the points pH zero charge corresponding to the catalyst and to the dye (in this order).

Photodegradation may be inhibited at higher concentrations of H_2O_2 because H_2O_2 can be adsorbed on the catalyst surface changing its catalytic activity.

Besides TiO_2 many other semiconductor materials are investigated, mainly transition metals oxides such as: ZnO , WO_3 , SnO , SrTiO_3 , $\alpha\text{-Fe}_2\text{O}_3$, SrO_2 , ZrO_2 [115].

Fe_2O_3 . These materials do not have high adsorption properties of the light energy, but they have a good chemical stability in aqueous medium and may have lower costs. The efficiencies of different catalysts in dyes degradation have been compared in recent studies. Some studies showed that ZnO and WO_3 are less efficient in azo dyes photodegradation. Tungsten trioxide (WO_3) has semiconductor properties, the band gap energy is equal to 2.6 eV, so it absorbs the light energy in ultraviolet and a small part in visible. The disadvantage of this photocatalyst is its solubility in average and extreme alkaline and acidic media [116]. Iron oxides in their polymorphs ($\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$, $\beta\text{-FeOOH}$, $\delta\text{-FeOOH}$ and $\zeta\text{-FeOOH}$) have the advantages of low cost but alone are unsuitable photocatalysts as they degrade rather easily [117]. Zinc oxide has the band gap energy equal to 3.2 eV, similar to anatase, but it is instable in aqueous solutions forming $\text{Zn}(\text{OH})_2$ at the catalyst surface, which leads to the catalyst deactivation [118].

All these oxides can be found in traces or in larger amounts also in fly ash, giving to this material a certain photocatalytic input.

The new materials with photocatalytic activity were preparation and tested for organic pollutants photodegradation such as multi-walled carbon nanotube-supported tungsten trioxide composite ($\text{WO}_3/\text{MWCNTs}$) [119] and multi-walled carbon nanotube-supported TiO_2 composite. Doping a small amount of MWCNTs may enhance photocatalytic activity of WO_3 [120] and of TiO_2 [121, 122] and these composite would have a widely applied with prospect in photocatalytic field. The reason may be: the large surface area of MWCNTs and different diameters of open end; can adsorb dye and oxygen on the inside and outside of the surface; the oxygen can get electron (e^-) from MWCNTs (are better electronic conductors) to form O_2^- ions, which not only enhance oxidation ability but also absorbs electron on the surface of MWCNTs; the UV light may enter the inner MWCNTs easily because of their open end.

Recent was obtained the photocatalytic porous ceramic materials $\text{TiO}_2/\text{fumed silica}$ [123] with high tensile strength (6.67-8.18 MPa), high surface areas (25.01-25.07 m^2/g), high anatase

content (>90%) and good photocatalytic activity confirmed by the complete degradation of a 10 mg/L methyl orange solution using UV light after 24 h.

The effect of light radiation intensity and radiation time

Experimental result of the studies investigating the effect of irradiation intensity on the kinetics of the photodegradation processes is described in Fig. 9 and shows that:

- at low irradiation densities (0-20 mW/cm²) the reaction rate increases linear with the increase of the intensity of the radiation, as the charged particles generation is the predominant process, following a first order kinetics (field I):

$$\ln \frac{c_0}{c} = k \cdot t ; \quad (25)$$

- at average illumination intensities, about 25 mW/cm², the reaction rate depends on the square of the light radiation intensity, and follows a 0.5 order kinetics (field II);
- at high illumination intensities the reaction rate is independent of the light radiation intensity. This can be explained by the fact that the process of electrons-holes generation compete with the recombination process, reaching equilibrium, with an apparent kinetic of order 0 (field III) *Langmuir - Hinshelwood model*.

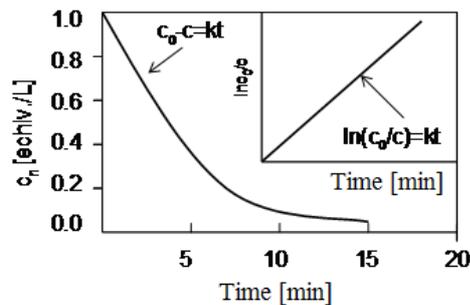


Fig. 9. The kinetic of photodegradation, Langmuir - Hinshelwood model

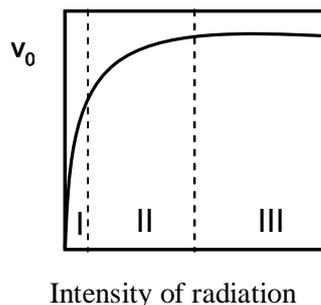


Fig. 10. The effect of light radiation intensity

I.7. Fly Ash - Low Cost, High Efficiency Adsorbent

I.7.1. Fly Ash a Waste

Escalating the volume of by-products generated by industrial progress, became a threat at planetary scale and requires concentrating attention for finding efficient and affordable solutions for mitigation or complete removal. In this context the European Commission for Environment and Development defined a new eco-politic model and introduced the term *Sustainable Development*. Sustainability has to start from the idea that all the human activities have significant effects on the environment and resources.

Modification of the ecosystems due to the production- consumption pattern based on economic progress (without meeting the environment needs) shows how important is rethinking the industrial processes by using/re-using the natural resources. Recycling for re-use is thus a topic that needs to be coherently addressed to and should focus particularly on wastes resulted in large amounts.

The secondary raw materials are those materials obtained after initial use and can be further repeatedly used in production as charge stock. The waste can be returned at a recycling technological process by *reuse*, in a totally different technological process for obtaining a new product. The waste can be described as a solid or liquid material with a complex composition with zero or negative economic value if is not reused or recycled.

Romania was among the first countries in the world which adapted at the state level, a new conception on the reuse of secondary raw materials in industrial processes.

As an energy source, coal is largely used worldwide in combined heat and power plants (CHP). The international Energy Agency reported that over 25% of the total energy demand is obtained based on coal burning, while the production of electric energy relies on coal and peat in a percentage that is over 40%.

The fly ash from power plants represents the main industrial waste after coal burning; due to its composition and properties this waste is a good candidate as second raw material, ensuring its technical and economy competitiveness now and in the future.

The first attempts to reuse fly ash are dating from 1930 in the U.S. The first company “Chicago Fly Ash Company” initiated the technology to introduce the ash in cement. In 1950 the American expertise was sent to Europe and then on other continents. Still, according to the statistics, at the level of 1987, about 376 million tons of fly ash was produced in the energy sector and only 16.5% was reutilized.

According to the American Coal Ash Association (ACAA), combustion of coal in the United States alone generated approximately 128,7 million tones of CCP in 2002, including approximately 76,5 million tones of fly ash, 19,8 million tones of bottom ash, 29,2 million tons of flue gas desulphurization (FGD) materials and 1,9 million tones of boiler slag [124]. From the fly ash produced, approximately 12,6 million tons were used in cement, and grout applications and another 14,1 million tones were used in various other applications.

In the following 10 years even if some countries have achieved remarkable results related to ash reuse (over 95% in Germany, 32% in the U.S, 47% in Australia and New Zealand, 40% in China) and 25% in India and the global reuse share in the world is below 25%.

Now-a-days, in some parts of the world, CCP utilization rates are much higher than that of the US. For example, in Netherlands CCP utilization is about 104% (Netherlands imports ash, as their supply is less than the demand). CCP utilization in Denmark is approximately 90% in Belgium over 73% and in other part of Europe the share varies from 10% to 60% [125]. At European level the share of reused fly ash is presented in Table 7:

Table 7. *Dynamics of ash production and reuse in Europe during 2003-2008 according to European Coal Combustion Products Association, ECOBA*

Year	The production of ash [millions of tones]	Amount of ash reused [millions of tones]	Share of reuse [%]
2003	44.21	21.11	47
2004	43.47	22.01	50
2005	42.75	20.93	48
2006	40.40	20.10	49
2008	37.47	17.69	47

Burning of coal in power plant has gone several process modifications to improve efficiency and the quality of air emissions, and to improve the chemistry of combustion products. Regulations to reduce sulfur dioxide emissions results in the introduction of wet scrubber flue gas desulphurization (FGD) systems which can produce gypsum as a by-product.

Fly and bottom ash recovery leads to numerous technical, environmental and social advantages, both for suppliers and consumers.

Depending on the fly ash characteristics, various areas for reuse were identified, Fig. 11.

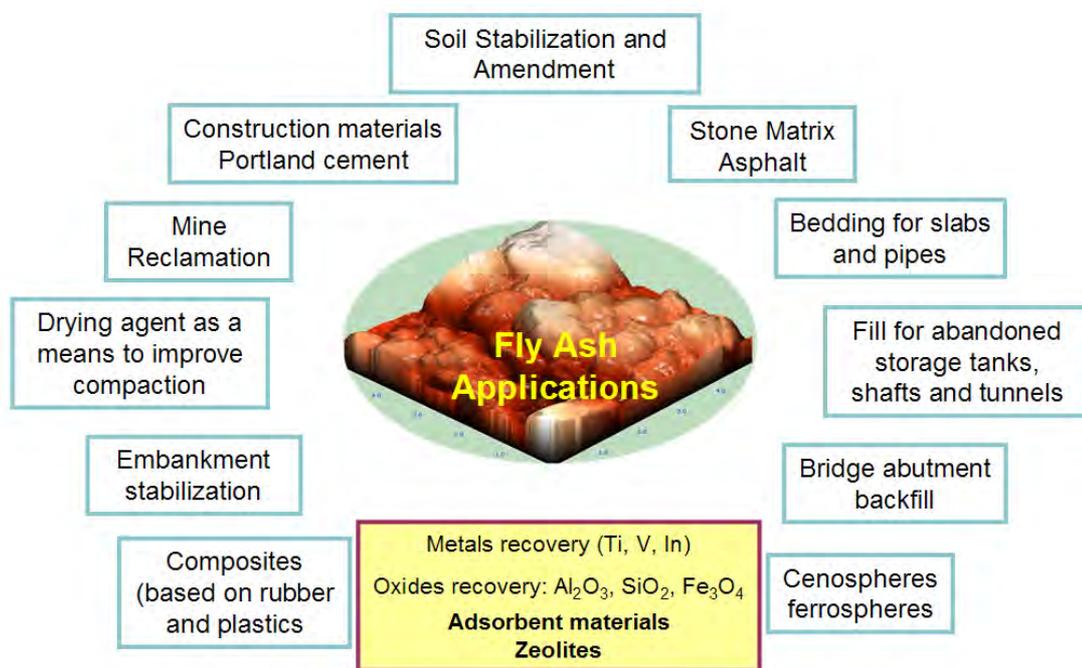


Fig. 11. Several applications of fly ash

In 1991 in Romania, about 97% electricity and 38% heat were produced by power plant using indigenous lignite coal resulting 11×10^6 t CCP, out of which 855 slag and bottom as and 15% fly ash. The large area of land occupied by ash and slag resulted from the 28 coal power plant is 2500 ha.

One of these CPHs is CET Brasov which works with two boilers (420 t/h capacity) and two turbo-aggregates that generate 50 MW/each. Every year 6×10^5 tons of coal is burned and the resulted fly ash is 2×10^5 tons/year. Part of the ash (1/3) is used in cement manufacturing but large amounts are still stored in free, open space and represent a major pollutions source. For this, and generally speaking for fly ash, there is a need to identify alternative processes of reuse.

I.7.2. Coal Combustion Products

Besides energy production, coal burning is responsible of huge amounts of wastes. The products of coal combustion (CCP) are materials that remain after the coal is burned: the boiler slag, bottom ash in the bottom of the combustion chamber and fine particles (fly ash) are removed from the flue gas by electrostatic precipitators and flue gas desulphurization materials. The fly ash represents more 65% of the CCP.

Depending on the type of fuel and combustion technology applied, various type of wastes result, encoded at European legislation, Table 8:

Table 8. *Types of wastes encode* [126]

Waste code	Type of waste (fly ash)
10 01 01	Bottom ash, slag and boiler dust (excluding boiler dust specified at 10 01 040)
10 01 02	Fly ash from coal burning
10 01 03	Fly ash from peat coal and untreated wood burning
10 01 04	Fly ash from oil and boiler dust burning
10 01 13	Fly ash from emulsified hydrocarbons used as fuel
10 0114	Bottom ash, slag and boiler dust from co-incineration of wastes with dangerous substances content
10 0115	Bottom ash, slag and boiler dust from co-incineration of other waste than those mentioned at 10 0114
10 0116	Fly ash from co-incineration of wastes with dangerous substances content
10 0117	Fly ash from co-incineration of other waste than those mentioned at 10 0116

Fly ash is a waste resulted from the rapid combustion of coal dust in boilers at 1200-1600 °C temperature with a high environmental impact and which has to be stored. The pulverized coal is burned in the furnace to generate heat. In large power plants which consume large quantities of coal, substantial quantities of coal ash are produced and collected in electrostatic precipitators or bag houses called fly ash (FA).

Bottom fly ash is formed when ash particles soften or melt and adhere to the furnace walls and boiler tubes. These larger particles agglomerate and fall to hoppers located at the base of the furnace where they are collected and often ground to a predominantly sand size gradation. The bottom ash share is in the range of 10-20%.

Boiler slag is formed when a wet-bottom furnace is used. The boiler slag represents the major component of cyclone boiler by - products (70 to 85%).

Flue gas desulphurization (FGD) material is the solid material resulting from the removal of sulfur dioxide gas from the utility boiler stack; the gases in the FGD process react with the slurred limestone or lime with to produce calcium sulfite which can be oxidized to synthetic gypsum.

Cenospheres are free - flowing powders (hollow spheres), with particle sizes of 50 μm and ultra-low densities (typically 0.7); they are extremely stable, do not absorb water, are resistant to most acids and are refractory materials that can resist at high temperature. Between 1% and 2% of the fly ash produced from the combustion of coal is formed as cenospheres with high silica content (55-61%) and lower calcium content (0.2-0.6%) in silicate glass. Cenospheres can be used in plastics, glass-reinforced plastic, light-weight panels. Because of their flexibility, they are used in many high-tech and traditional industries including: aerospace; hovercraft, carpet baking, window glazing; putty etc.

All over the world, there are numerous studies on the characterization and exploitation of fly ash, extending the traditional path represented by the reuse in Portland cements manufacturing, based on pozzolanic activity of the fly ash [127]. However, recovery of this waste represents a problem that is far from being fully solved.

I.7.3. Fly Ash Composition and Characterization

Fly ash is called “flying” as it is transported from the combustion chamber by exhaust gases.

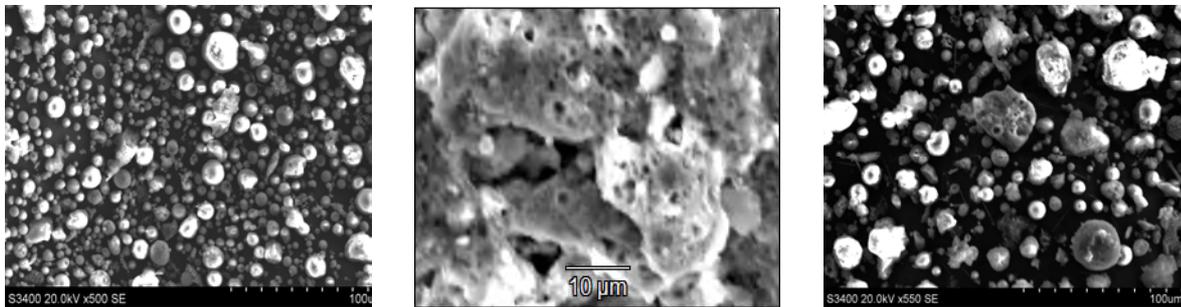
Fly ash is a fine powder, abrasive, mostly alkaline, refractory in nature, usually grey or yellowish-brown, Fig. 12, composed of coal mineral matter plus a small amounts carbon resulting from incomplete combustion (called “loss of ignition”).



Fig. 12. *The color of fly ash*

The color of fly ash depends on the coal type and composition and on the burning conditions. The grey dark color of fly ash outlines a large amount of unburned carbon, while a light-grey color means a large amount of lime. The brown color of fly is the result of a large amount of iron oxides. The specific gravity of the fly ash usually ranges from 2.1 to 3.0 and the specific surface area may vary from 170 to 1000 m²/kg [83].

The fly ash particles are very fine, having shapes ranging from predominant spherical up to shell agglomerates, Fig. 13.



Fly ash from Mintia Deva

Fly ash from CET Brasov

Fly ash from CET Craiova

Fig. 13. *Scanning electron micrographs of the fly ash in the particle size range of 10 to 150 µm [128]*

Spheres of many different sizes and surfaces are found either loose or embedded in a larger matrix-like structure. At higher magnification shown in Fig. 13 the matrix appears to be a conglomeration of spherical particles with different sizes.

The average particle size is about 10 µm but can vary from 1 µm at over 200 µm, with various grain size distribution curves Fig. 14.

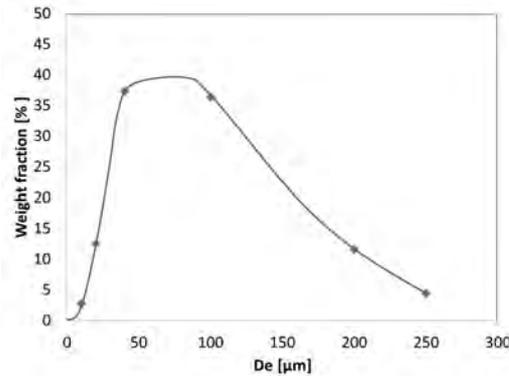


Fig. 14. Particle size distribution (Granulometry curve) [129]

The largest fractions of fly ash particles have diameters between 40 and 100 μm . Some deviation must exist for these values due to the conglomeration of some smaller particles. Clustering of the smaller particles was observed in SEM micrographs of fly ash powder collected in a larger particle size range, thus confirming that such conglomerates may be retained by coarser mesh sizes.

Not only the color but also the overall composition of the fly ash is very different and depends on the type of coal used, grinding equipment, furnace geometry and the combustion process itself, Table 9.

The majority of minerals from coal are: aluminosilicates, silica (quartz), sulphides and carbonates which during combustion some minerals (clays) are changed at high temperature while other minerals such as quartz may remain unchanged.

Table 9. Normal range of chemical composition for fly ash produced from different coal types [125]

Compounds	Bituminous Coal	Sub-bituminous coal	Lignite
SiO ₂	20-60	40-60	15-45
Al ₂ O ₃	5-35	20-30	10-25
Fe ₂ O ₃	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO ₃	0-4	0-2	0-10
Na ₂ O	0-4	0-2	0-6
K ₂ O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

According to American Society for Testing Materials (ASTM 618-03), fly ash is classified into two classes: class F fly ash and class C., Table 10. The difference between these two classes is the amount of silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO) and iron oxides.

The Class C fly ash results from the burning of lignite coal, and cements when the water is added. The $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content is between 50...70%.

The Class F fly ash results from burning bituminous coal (pit coal), and don't cement when the water is added. A pozzolanic material is reinforced with water only in the presence of an alkaline material such as lime. Class F fly ash normally contains less than 5% CaO. The $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content is above 70%.

Table 10. Typical chemical composition of fly ash class F and class C [125]

Compounds	Class F fly ash		Class C fly ash		Portland Cement (Lafarge Corporation)	
	Typical	ASTM C-618	Typical	ASTM C-618	Typical	ASTM C-150
SiO_2	36.9	-	41.36	-	20.25	-
Al_2O_3	18.1	-	21.83	-	4.25	-
Fe_2O_3	3.6	-	5.56	-	2.59	-
$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	58.6	70.0 (min %)	68.75	50.0 (min%)	27.09	-
CaO	2.85	-	19.31	-	63.6	-
MgO	1.06	-	3.97	-	2.24	6.0 (max %)
SO_3	0.65	5.0 (max %)	1.42	5.0 (max %)	-	3.0 (max %)
LOI	33.2	6.0	0.8	6.0	0.55	3.0 (max %)
Moisture contents	0.14	3.0 (max%)	0.01	3.0 (max %)	-	-
Insoluble residue	-	-	-	-	-	0.75 (max%)
Available Alkalies as equivalent Na_2O	1.36	-	1.64	-	0.29	-

These types of fly ash from coal power stations can be used to produce glass-ceramics composite, the potential material for producing diffusers which could be used for water aeration [130] and for wastewater treatment.

Fly ash also contains different essential elements such as: macronutrients P, K, Ca, Mg and micronutrients Zn, Fe, Cu, Mn, B and Mo for plants growth but is possible to contain and toxic elements such as: arsenic, mercury, and lead in small percents.

The mineralogical composition of fly ash has depended on geological factors related to the age of coal, geological area, type of coal (anthracite, bituminous coal, lignite, brown coal), combustion conditions and can be established by X-ray diffraction analysis (XRD).

The X-ray diffraction (XRD), Fig. 15 shows that predominant mineral phases are crystalline and the major components are: SiO_2 (as αSiO_2 quartz, quartz syn and tetragonal and orthorhombic SiO_2) combined with Al_2O_3 (as rhombo H, mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_5$ and $\gamma\text{-Al}_2\text{O}_3$), iron oxides (hematite Fe_2O_3 and magnetite Fe_3O_4), the less MnO_2 , lime (CaO) and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The particle size of mullite produced by the decomposition of kaolinite may be as small as 0.01.

The unburned carbon graphite and carbon hexagonal (chaoite), along with compounds as micro-sized crystallites represents a significant part of the substrate and can explain the versatility of this material in adsorption processes of heavy metals, organic pollutants, including dyes and surfactants [128].

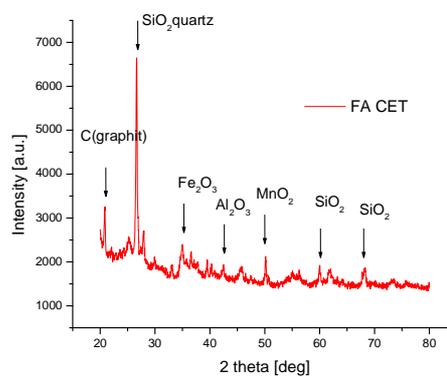


Fig. 15. XRD graph of FAw

Based on this type of data the empirical formula can be:



At many CPHs from Romania the fly ash is of class F according to the composition provided by the companies Table 11.

Table 11. *The composition of the raw fly ashes collected from CPHs in Romania [128]*

CPHs	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	SO ₃ ²⁻	LOI*	% ^{**} SiAlFe
1	53.32	22.05	8.97	5.24	2.44	2.66	0.63	1.07	0.08	0.12	1.40	1.58	86.34
2	46.13	21.39	10.85	10.65	5.24	0.5-2	0.2-0.6	<1%	-	-	-	-	78.37
3	50.33	23.37	9.27	7.32	2.32	-	0.63	1.07	0.08	2.95	2.19	1.39	82.79
4	46.05	20.08	9.93	6.07	2.35	2.28	0.83	0.06	0.09	-	-	4.45	76.06

1. CET Braşov SA; 2. CET Govora SA; 3. S.E. Hunedoara Deva (Mintia); 4. S.E.CRAIOVA II.

The values indicate a uniform composition with predominantly major oxide compounds.

The total share of major components (SiO₂, Al₂O₃, Fe₂O₃) is in each case more than 75% (thus is of F class), and will not aggregate in water. This poses a major environmental problem in storage but is a significant advantage when seeking use of particulate dispersions. Another interesting component in the ash composition is P₂O₅ (in small amount in the CET Braşov fly ash and in a larger share in the CET Govora compound) and this can affect further processing. Trace elements (B, Cu, Zr, Sn, Pb, As, Ni, Zn, Ti, Cr, V) are in magnitude order of ppm but have a significant contribution to the harmful effects on the environment (toxic leachate). The retention of hazardous elements by fly ash produced in combustion plants has been extensively studied in recent years. Besides flue gas desulfurization (DFG) the mercury has been observed at some fly ash and which would otherwise be emitted into the atmosphere. The concentration of unburned carbons and their respective ability to capture Hg have also been related to their textural properties, given that BET surface area successively increased from isotropic coke (isotropic fly ash carbons) to anisotropic coke (anisotropic fly ash carbons) [83].

The composition, surface area and presence of unburnt carbon (2-12%) play an important role in determining the application.

These four types of fly ash were collected and reused as adsorbents in advanced wastewater treatment, including for obtaining of zeolites materials (the project: **New adsorbents of zeolite type obtained from waste fly ash collected from Romanian Combined Heat and Power Plants, PN - II- RU-TE-2013-3-0177, grant coordinated by Maria Visa**).

As being a mixture of metal oxides and unburned carbon, fly ash has a charged surface that makes it suitable for adsorption. Most of the meta-oxides are negatively charged, thus fly ash can be a good adsorption substrate for cations (e.g. heavy metals) removal. Additionally, the grain-structure and potential convenient specific surface supports the fly ash reuse in adsorption processes.

Further on, fly ash is primarily composed of aluminosilicate glass, mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and quartz (SiO_2). These materials provide a ready source of Al and Si, which in an optimized ratio can represent potential precursor for the synthesis of zeolites. These zeolites or zeolite-type materials are likely to represent even better adsorbents that can be tailored for selective removal processes.

I.8. Fly Ash - Adsorbent in Wastewater Treatment

Fly ash represents an environmental threat, due to the small particles that can raise PM_{10} and $\text{PM}_{2.5}$, and the leachate that is highly toxic. Although industrial reuse is already implemented, the FA amounts are far larger than the recycled amounts, therefore novel recycling solutions are continuously searched for. During the past five years over 7000 papers were indexed in ISI Thompson Web of Science, dealing with this topic, among which, over 1400 were published in 2011.

Considering its generic composition, FA can also be used as adsorbent, particularly in wastewater treatment also reducing the threats for air and water pollution.

I.8.1. Fly Ash - Adsorbent for Heavy Metals

With the growth of population, society, science and technology our world is connected to new high horizons but the cost which we will pay in near future will be too high. The consequences of this rapid growth are environmental disorder with many pollution problems. The demand of water has increased for agricultural, industrial and domestic sectors and result a large amounts of wastewater containing a lot of dangerous pollutants.

One important pollutants class is represented by *heavy metals*.

The conventional techniques used for heavy metal removal are expensive and with average efficiency. The most commonly used methods for heavy metal ions removal are: chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electro-dialysis, electrolytic extraction, reverse osmosis, ion-exchange, cementation, dilution, flotation, flocculation, sedimentation, soil flushing/washing chelating etc. For example, at industrial scale the ion-exchangers and activated carbon are used but there are certain disadvantages. The activated carbon is a great adsorbent for organics but the efficiency in heavy metals removal is average and de-sorption and regeneration is difficult under common conditions, thus the overall process becomes expensive. Ion-exchange is an efficient method, with moderate selectivity since it can not only remove the heavy metal ions but exchange the Ca^{2+} , Mg^{2+} ions, thus reducing the effective capacity. Supplementary, the ion exchangers can load with organics, thus modifying the surface and decreasing the process reversibility. These adsorbents are efficient but do not represent a fully sustainable option, as most of the commercial ion exchangers are obtained from oil derivatives, in energy-consuming processes.

Still, adsorption is an efficient process which can use various biological materials, mineral oxides, activated carbon, resins even waste materials. Many researches had investigated the adsorption capacity of less expensive materials such as red mud, natural zeolite, wood based biosorbents, scrap rubber, bituminous coal, peat, sugar beet pulp, marine alga *Padina* or bone char etc. for heavy metals (cadmium, cooper, zinc, nickel, iron) removal.

The fly ash is a low cost waste material which can be an efficient substrate in wastewater treatment for the immobilization of heavy metals, mainly Cd^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , Hg^{2+} , Cr (VI), Cr (III). Using fly ash may be involved two processes: adsorption and precipitation of the heavy metals. *Precipitation* of heavy metal results from presence of calcium hydroxide $\text{Ca}(\text{OH})_2$, that has remained after desulphurization and *adsorption* due to present of silica, alumina in fly ash.

The use of fly ash for removal heavy metals from wastewater was reported as early as 1975 (Gangoli et al.). Since then, many research groups focused on optimizing the efficiency of fly ash - based adsorption processes. Table 12 summarizes the results of the most important pollutant/toxic metals investigated using fly ash.

Table 12. Summary of reports on metals adsorption on fly ash [83]

Metal cations [M ^{Z+}]	Adsorbent	Adsorption capacity [mg/g]	Temperature [°C]	References
Cu ²⁺	Fly ash (FA)	1.39	30	[131]
	FA + wollastonite	1.18	30	[132]
	FA	1.7-8.1	-	
	FA (I)	0.34-1.35	20	[133]
	FA (II)	0.09-1.25	20	
	FA	207.3	25	[134]
	FA - washed	205.8	25	[135]
	FA - acid	198.5	25	
	FA	0.63-0.81	25	
	Coal Fly Ash (CFA)	20.92	25	[136]
	CFA-600	126.4-214.1	30-60	[137]
	CFA-NaOH	76.7-137.1	30-60	
	FA	0.76	32	[138]
Pb ²⁺	FA	444.7	25	[134]
	FA - washed	483.4	25	
	FA - acid	437.0	25	
	FA	752	32	
	FA	18.8	-	[139]
	FA zeolite	2000	25	[140]
Cd ²⁺	FA	198.2	25	[134]
	FA zeolite	30.21	25	[140]
	FA zeolite	95.6	20	[141]
	FA	0.67-0.83	20	
	FA (I)	0.08-0.29	20	[142]
	FA (II)	0.0077 -0.22	20	
	FA	198.2	25	
	FA - washed	195.2	25	[132]
	FA - acid	180.4	25	
	FA	1.6-8.0	25	
Ni ²⁺	FA	9-14.0	30 -60	[143]
	FA impregnated with Fe	9.8-14.93	30 -60	
	FA impregnated with Al	10-15.75	30 -60	
	FA (I)	0.40-0.98	20	[143]
	FA (II)	0.06-1.16	20	

Metal cations [M ^{z+}]	Adsorbent	Adsorption capacity [mg/g]	Temperature [°C]	References
Zn ²⁺	CFA	6.5-13.3	30-60	[143]
	FA impregnated with Fe	7.5-15.5	30-60	
	FA impregnated with Al	7.0-15.4	30-60	
	FA	0.25-2.8	20	[134]
	CFA (I)	0.25-1.19	20	[144]
	CFA (II)	0.07-1.30	20	
	FA	7.84	25	[145]
	FA	4.64	23	[146]
	FA	0.27	25	[147]
	FA	0.068-0.75	0-55	[147]
	FA zeolite	18.87	25	[140]
Cr ³⁺	FA	52.6-106.4	20-40	[148]
Cr ⁶⁺	FA + wollastonite	2.92	-	[149]
	FA+ China clay	0.31	-	[150]
	FA	1.38	30-60	
	FA impregnated with Fe	1.82	30-60	[151]
	FA impregnated with Al	1.67	30-60	
	FA (I)	0.55	20	[151]
	FA (II)	0.82	20	
Hg ²⁺	FA	2.8	30	[152]
	FA	11.0	30-60	[151]
	FA impregnated with Fe	12.5	30-60	
	FA impregnated with Al	13.4	30-60	
	Silico-aluminous ashes	3.2	30	[153]
	FA class C	0.63-0.73	5-21	[153]
As ³⁺	Fly ash coal-char	3.7-89.2	25	[154]
As ⁵⁺	Fly ash coal-char	0.02-34.5	25	[154]
	FA	7.7-27.8	20	[155]

Removal the heavy metals cations on fly ash or other solid substrate obtained from mixture of fly ash with lime, bentonite, diatomite or wollastonite was investigated optimizing the effects of contact time, dosage of substrate, initial concentration of the heavy metals, and adsorption capacity of the fly ash that is activity of the specific surface area, pH and temperature.

The adsorption process is exothermic, so high temperature doesn't favor the adsorption of heavy metals.

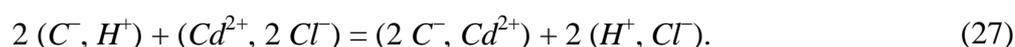
Raw fly ash and modified coal fly ash are good adsorbent for the removal copper cations. The adsorption of Cu^{2+} cations were endothermic in nature [137] occurs with activation energy (1.3 at 9.6 kJ/mol) consistent with ion exchange adsorption mechanism.

The alkaline pH of solution can favors the removal of heavy metals till a value of pH and up to a certain value; depend of the heavy metal, and then the efficiency decreased.

The maximum removal is observed at pH = 8.

Fly ash with different quantities of carbon and minerals were used as adsorbents investigating the contribution of precipitation and adsorption to the removal the copper cations. Present of carbon in fly ash increase the adsorption capacity from 2.2 to 2.8 mg Cu^{2+} /g carbon, while in present of mineral value was only 0.63-0.81 mg Cu^{2+} /g mineral. The author shows that: removal Cu^{2+} cations is enhanced owing to precipitation in the same time decrease with carbon fraction of fly ash and was estimated at 23-82%.

The processes can be descried with these equations related to the cation adsorption from aqueous solutions:



Mercury removal by adsorption is optimum at pH between 5.0-5.5 and the adsorption process is endothermic.

The removal of Cd^{2+} , Cr^{3+} , Ni^{2+} , Zn^{2+} cations from wastewater on fly ash was investigated by Viraraghavan et al. at different conditions: contact time, dosage, pH and temperature.

The alkaline between pH 7-8 favors the adsorption of cadmium from aqueous solution while for chromium the maximum adsorption is at range of 2.0-3.0 and for Ni^{2+} , Zn^{2+} the range of pH which favor the adsorption is 3.0-3.5.

The high efficiency of adsorption depends on the nature electric charges off the surface of the adsorbent, the shape of pores and the adsorption sites which increased with adsorbent dosage. The adsorption may be decrease if the particles aggregation and then the active sites decrease.

The adsorption capacity of fly ash depends on the surface activities (surface interaction), thus for heavy metals it depends on the equilibrium between competitive adsorption of all the cations, their ionic size and stability of bonds between heavy metals and alumino-silicate or calcium silicate hydrates.

The adsorption of heavy metals cations can be significantly affected by the organic pollutants. Wang et al. [156] investigated the adsorption of copper and lead in presence of humic acid (HA) on fly ash, and found a competitive adsorption between copper and lead with a better adsorption capacity in presence of humic acid, increasing from 18 mg/g in single pollutant system to 28 mg/g Cu^{2+} in Cu-HA and for Pb^{2+} increase from 7 mg/g to 37 mg/g in the system Pb-HA, as the humic acid developed new active sites which favor the adsorption of heavy metals.

Generally, removal efficiency of toxic heavy metals from water using fly ash is in agreement with the order of insolubility of the corresponding metal hydroxides, $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$.

The adsorption capacity can be enhanced by modifying the fly ash substrate.

Banerjee et al. [143, 152] observed that adsorption of Ni^{2+} , Zn^{2+} , Cr^{3+} and Hg^{2+} on fly ash impregnated with Fe and Al showed much higher adsorption capacity compared to untreated fly ash.

Other groups investigated the adsorption of heavy metals Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} on fly ash mixed with lime in different proportion. The calcium silicate hydrated is responsible for enhanced the removal of heavy metals by adsorption in the order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$.

The fly ash is a waste used for the removal of arsenic from wastewater and the radionuclides of ^{90}Sr and ^{137}Cs . Suggested mechanism of retention of radionuclide by fly ash is specific adsorption of Cs(I) and irreversible ion exchange uptake of Sr(II).

I.8.1.1. Adsorption Isotherms and Uptake Kinetics of the Heavy Metals

The heavy metals adsorption mechanisms were investigated based on the isotherms, using the Langmuir [151] and Freundlich [157] Equations, Eq. (28) and (29):

- The Langmuir isotherm (linear form of the Eq.):

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{q_{max} a} + \frac{c_{eq}}{q_{max}} \quad (28)$$

The adsorption mechanism may be modelled with Langmuir isotherm for heavy metals adsorption on homogenous surfaces without interaction between adsorbed molecules.

- The Freundlich [157] isotherm (linear form of the Eq.):

$$\ln q_{eq} = \ln k_f + \frac{1}{n} \ln c_{eq}, \quad (29)$$

were the k_f - is Freundlich constant, the measure of adsorption capacity and $1/n$ is a dimensionless parameter indicating the adsorption intensity.

Adsorption phenomena observed at various heavy metals cations removal on fly ash/modified fly ash were modelled also by other isotherms: Redlich-Peterson, Dubinin-Kaganer- Radushkevich, Tempkin and Sips isotherms.

The Redlich-Peterson (R-P) isotherm describes the adsorption process on heterogeneous surface by the β parameter with value between $0 < \beta < 1$:

$$q_{eq} = \frac{A \cdot C_{eq}}{1 + BC_{eq}^\beta}, \quad (30)$$

where: C_{eq} - is the equilibrium concentration [$\text{mg} \cdot \text{L}^{-1}$] of heavy metal; A and B are the R-P constants, β is a dimensionless parameter of R-P heterogeneity. If the $\beta = 0$ the R-P equation represent the Henry Equation and if the $\beta = 1.0$ the Eq. (30) reduces at the Langmuir isotherm.

The isotherm Equation of Dubinin-Kaganer-Radushkevich (DKR) is:

$$\ln Q_{eq} = \ln Q_m - \beta \varepsilon^2, \quad (31)$$

where: Q_{eq} is the amount adsorbed (mol/g), Q_m (mol/g) is the monolayer capacity; β (mol²/J²) is a constant related to the adsorption energy; ε is the Polanyi potential related to the equilibrium concentration through the Eq. (32):

$$\varepsilon = RT \ln 1/C, \quad (32)$$

where T is the temperature and C is the equilibrium concentration of the adsorbate in solution.

The thermodynamic parameters standard free energy change (ΔG^0), standard enthalpy (ΔH^0) and standard entropy change (ΔS^0), may be calculated using the following Eq. (33):

$$\ln K_c = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \quad (33)$$

where the K_c is the equilibrium constant.

The $\ln K_c$ versus $1/T$ plot is used to calculate the thermodynamic parameters (ΔG^0), (ΔH^0) and (ΔS^0).

The negative value of ΔG^0 proves that adsorption is spontaneous, while the negative value of ΔH^0 confirms the exothermic phenomena and ΔS^0 is used to describe the entropy/randomness at the solid-solution interface during adsorption.

The Sips model proves that the equilibrium data follow Freundlich curve at lower concentration and follows Langmuir model at higher concentration. The Eq. is:

$$Q = (K_s \cdot C_e)^\beta / [1 + (\alpha_s \cdot C_e)^\beta], \quad (34)$$

where K_s (L/g) and α_s (L/mg) are Sips isotherm constants and β is the exponent which lies between 1 and 0.

Uptake kinetics of the heavy metals

The steps which are followed in adsorption process are:

- transport of the solute from bulk solution through liquid film to the adsorbent exterior surface;
- solute diffusion into the pore of adsorbent except for a small quantity of sorption on the external surface ; parallel to this is the intra-particle transport mechanism of the surface diffusion;
- sorption of the solute on the interior surface of the pores and capillary spaces of the adsorbent.

Three well - known kinetics models are reported to fit the experimental kinetics data: pseudo-first - order, pseudo-second - order and inter-particle diffusion.

- The pseudo first-order Eq. Lagergren, 1898 [158]:

$$\log (q_e - q_t) = \log (q_e) - \frac{K_L}{2.303} t, \quad (35)$$

K_L is the Lagergren constant, q_e is the equilibrium uptake value and q_t the current pollutants uptake.

- The pseudo-second order kinetics (Ho and McKay, 1999) [159, 160] was found to best model the experimental data in heavy metals adsorption, Eq. (36):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (36)$$

where k_2 is the pseudo second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

- The inter-particle diffusion, that usually runs parallel with other mechanisms, in the very narrow pores [161]:

$$q = k_{id} t^{1/2} + C, \quad (37)$$

where k_{id} is the rate constant and C is an adjustable parameter.

After adsorption the fly ash can be regenerated using non toxic reagents. The saturated fly ash was regenerate with aqueous solution of H₂O₂ 2%.

I.8.2. Fly Ash - Adsorbent for Dyes

One of the important classes of pollutants is represented by dyes which once discharged in the water are very difficult to treat as result of their complex, stable molecular structure.

Mankind has used dyes for thousands of years and the earliest known user of colorants is believed to be the Neanderthal Man. However the first known use of organic colorants was much later, nearly 4000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs [162]. Till the nineteenth century, the dyes were naturally prepared on small scale, from fruits or leafs plants as main sources. Only starting with 1856, after the Perkin`s historic discovery of the firs synthetic dye, mauveine, that dyes were synthetically manufactured on a large scale [163].

Any dye molecule consists of two components: *the chromophores* group (–N=N– and anthraquinone), responsible for producing the color, and *the auxochromes* which can not only supplement the chromophore but also render the molecule soluble in water and enhances the ability to attach toward the fibers.

Dyes can be classified considering different criteria: chemical structure, solubility or type of fiber on which it can be applied. Water-soluble dyes include acid, mordant, metal complex, direct, basic (cationic) and reactive dyes, while water-insoluble dyes can be azoic, vat sulfur and disperse dyes. The one most widely used are the azo dyes.

A large variety of dyes are extensively used in the textile industry, leather tanning industry, paper production, hair colourings and food technologies. Over 10,000 dyes are currently used and more than 280,000 t of these are yearly discharged worldwide [164].

Azo-, antrachinone-, thiazine- and metal-complex dyes are well-known for their toxicity, some of them being proved as carcinogenic for animals and humans; as pollutants, they affect water transparency, reducing light penetration and gas solubility in water [165], and are

slowly or non-biodegradable [166, 167]. The major environmental problem when using reactive dyes is their loss during the dyeing process, because the efficiency of the fixation process is about 60-90% [168]. The resulted wastewaters exhibit therefore high BOD and COD values (above 2000 mg O₂/L) while the discharge limits are much lower (BOD < 40 mg O₂/L; COD < 120 mg O₂/L), indicating the need for specific wastewater treatment.

Since initially there was no discharge limit, the treatment of dye-polluted wastewater started just with some physical treatments such as sedimentation and equalization to adjust the pH, total dissolved solids (TDS) and total suspended solids (TSS) of the water discharged. Now-a-days, the recommended steps in dyes-polluted wastewater treatment are:

- *pre-treatment*: equalisation and neutralization;
- *primary treatment*: targeting pollutants removal, for minimizing the effort in municipal plants, by enhancing gravity settling of suspended particles with chemical coagulants/flocculants or by filtration.

The aluminium (Al³⁺), ferric (Fe³⁺) ions involve the flocculation of dye molecules [169]. In this case the sedimentation is faster. The main disadvantages are: the high cost of chemicals and the final product (a concentrated sludge) produced in large quantities; additionally, dyes removal is pH dependent. This process has poor efficiency in soluble dyes removal.

- *secondary treatment* usually involves microorganisms (*biological treatment*), primarily bacteria which stabilize the waste components. The processes can be: (a) *aerobic* (using oxygen; (b) *anaerobic* without oxygen and (c) *combined aerobic -anaerobic*.

In *aerobic* conditions the enzymes secreted by bacteria and fungi degrade the organic dyes as crystal violet, malachite green, pararosaniline all with three aromatic rings [170].

Similar studies on *anaerobic* treatment of textile effluents proved the advantages of this type of treatment: the dyes can be efficiently bleached in a low cost BD removal process, heavy metals (if any) can be retained through sulfate reduction, there is no foaming even when surfactants are part of the system, high effluent temperatures can be favourable, high pH effluent can be acidified and degradation of refractory organics can be initiated.

Combined aerobic-anaerobic treatment for dyes removal has several advantages: the dyes can be fully decomposed by mineralization, due to the synergic action of different organisms.

Studies showed that there is no universal removal process: the reduction of azo bond can be done under the reduction conditions (anaerobic processes, anaerobic bioreactors), while the aromatic amines may be mineralized under aerobic conditions. Thus, for complex-polluted wastewater several disadvantages of the bio-chemical processes are: less flexibility in design and operation, larger land area requirement and longer times required for bleaching-fermentation processes [171].

- *tertiary treatment* involves physical and/or chemical processes and includes: adsorption, ion-exchange, stripping, chemical oxidation, and membrane separations. All of these are more expensive than the biological treatment but are effective in the removal of very persistent pollutants.

The final step is the sludge processing and disposal. Wastewater load with dyes are also treated in more or less a similar way, nevertheless, there is no single standard treatment procedure used for all types of wastes.

Suspends solids (TSS) can be removed also by physical processes, including microfiltration, ultrafiltration, nanofiltration and reverse osmosis. *Microfiltration* is not much used (larger membrane pores as compared to the dyes molecules) but, using *ultrafiltration* and *nanofiltration* all classes of dyes can be removed; the disadvantage is that dye molecules can clog the membrane pores making the separation systems of limited use for textile wastewater. Other disadvantages are the high cost of membranes and a relatively short membrane life, high working pressures, significant energy consumption.

Adsorption has been widely used for dyes removal.

Adsorption refers to the process when the pollutants from liquid or gaseous are concentrated to a solid surface of the substrate. If the solid surface and the adsorbed molecules (dyes) are involved in physical interactions, such as van der Waals forces, the adsorption is called *physiosorption*. In this case the forces are weak and the desorption is easy, thus the substrate can be reused without imposing highly different conditions as compared to the direct (adsorption) conditions.

On the other hand if the attraction forces are due to chemical bonding (strong bonds), the process is called *chemisorption*; desorption occurs in this situation in more different conditions from the regular adsorption.

Adsorption process on porous carbons was described as early as 1550 B.C. in an ancient Egyptian papyrus and later by Hippocrates and Pliny the Elder, mainly for medical purposes.

Further observations related to adsorption were made by Lowitz in 1785 for the reversible removal of color and odor producing compounds, from water by wood charcoal. Later on, Larvitz in 1792 and Kehl in 1793 observed similar phenomena with vegetable and animal charcoals [57, 163].

A particular type of chemisorption is the ion exchange, a reversible process where an ion (anion or cation) from solution is exchanged for a similarly charged ion attached to a solid particle. Ion exchanges were used to remove colors, but the largest application of ion exchange [172] is for drinking water treatment, in calcium, magnesium, and other polyvalent cations removal, in exchange processes with Na^+ or H^+ . Various studies have been carried out using ion exchange for dyes removal [173, 174]. Synthetic ion exchangers are organic resins, e.g. polystyrene sulfonate, sulfonated phenolic resin, phenolic resin, polystyrene phosphonate, polystyrene amidoxime, polystyrene-based trimethyl benzylammonium, epoxy-polyamine and aminopolystyrene on which exchange groups are grafted. A number of exchange resins have been used quite efficiently for the removal of dyes [175, 176, 177].

One of the most important characteristics of an adsorbent is the adsorption capacity (i.e. the maximum amount of adsorbate accumulated on a given amount of substrate), that can be calculated from the adsorption isotherms. The adsorption isotherms are constant-temperature equilibrium relationships between the amount of adsorbate per unit of adsorbent (q_e) and its equilibrium solution concentration (C_e). Several equations or models are available that describe this function, but for dyes and heavy metal removal the mostly used are the Freundlich and the Langmuir equations. Dyes that are difficult to biologically decompose can be removed by using the porous adsorbents with high specific surface area.

Some of the adsorbents that are generally used for wastewater treatment loaded with dyes are: *alumina*, a synthetic porous crystalline gel of Al_2O_3 with surface area of 200...300 m^2/g [178, 179, 180], and *silica gel* (SiO_2) with large surface area of 250...900 m^2/g , prepared by the coagulation of colloidal silicic acid.

In 1977, research investigated the adsorption of basic dyes onto silica, outlining high adsorption capacities but the disadvantages was that high cost of the silica [159].

Zeolites, are important micro-porous adsorbents, which are found as natural compounds or are synthetically prepared. They are also considered as selective adsorbents and show ion exchange properties [181] as well as molecular adsorption features. Zeolites are largely used dyes removal; [182], along with other pollutants [183].

Activated carbon is the oldest adsorbent known and is usually prepared from coal, or biological materials with high content of the carbon as: coconut shells, wood, seeds etc., using one of the two basic activation methods: physical or chemical using chemical agents $ZnCl_2$, $MgCl_2$, $CaCl_2$, H_3PO_4 .

Activated carbon has a porous structure with large specific surface area (500 to 2000 m^2/g) with diameter of porous of 20-100 Å and with porosity up to 80%. The activated carbon is available in two main forms: as powdered activated carbon (PAC) and as granular activated carbon (GAC), the latest being mostly used in pollutants removal from wastewater because is no need to further separate the carbon from the bulk liquid.

The activated carbons which are used as adsorbents, not only remove different types of dyes [184] but also other organic and inorganic pollutants such as metal ions [185], phenols [186], pesticides, humic substances [187], detergents [188], organic compounds which cause taste and odor and many other chemicals [189].

Studies have shown that activated carbons are good materials for the removal of different types of dyes in general but their use is restricted by cost.

The carbon-based adsorption is therefore further investigated in other adsorbents with lower costs. A waste with a lower percentage of carbon is the fly ash. A number of researcher have attempted to use fly ash as an adsorbent to remove the cationic and anionic dyes Viraraghavan and Ramakrishna (1999) [190], as being a good combination of carbon (with eak surface charge) and oxides (with an overall negative surface charge).

Fly ash a waste/by-product material, is generally available free of cost and is produced in huge amounts from coal burning, in the central heat and power plants (CPH). It is the fine grained fraction, collected in the electrofilters and about 60% of it is used in concrete manufacturing [83]. Recent studies, show that various fly ash samples with different un-burnt

carbon contents collected from CPH, can be used for sequential adsorptions of basic dye, Methylen Blue (MB) [191, 192], Crystal Violet, Methyl Orange, basic dyes and CI Reactive Red 49 in aqueous solution, because the main components in fly ash act as active sites in dyes' adsorption. Wang et al. [192] also used fly ash as adsorbent for the removal of basic dye, (MB), from aqueous solutions and the adsorption capacity for raw fly ash was reported to be $1.4 \cdot 10^{-5}$ mol/g.

Many papers report on the dyes adsorption on fly ash in optimized conditions:

- Fly ash as low-cost adsorbent has been investigated by Mohan et al. [193] for the removal of cationic dyes crystal violet (basic violet) and rosaniline hydrochloride (basic fuschin). The fly ash resulting in Turkey was tested as adsorbent to remove three reactive azo dyes [Remazol Blue (RB), Remazol Red RB 133(RR) and Rifracion Yelow HED (RY)] [194]. The authors have investigated the effects of adsorbent dosage, contact time, particle size, pH, temperature, initial concentration and notated that adsorption of dyes increases with increasing temperature, thereby indicating the process to be endothermic in nature, Mohan et al. The removal of dye was found to be inverse proportional with the size of the fly ash particles and the results obtained by the workers indicated that the Freundlich adsorption isotherm fit the data better than the Langmuir adsorption isotherm.
- The effect of physical (heat) and chemical treatment was also investigated on as-received fly ash and the heat treatment was reported to have a small influence on the adsorption capacity of fly ash (as expected, considering that fly ash is the result of a high-temperature burning process), but alkaline treatment using NaOH, KOH, Ca(OH)₂ or acid treatment (HNO₃) resulted in an increase of the adsorption capacity of fly ash, mainly as result of morphology changes, with an increase in roughness and as result of developing a high surface charge. The works reported that the dye adsorption process on fly ash respects a first order kinetics (adsorption of crystal violet) or pseudo-second-order kinetic model (adsorption of Congo Red, MB) and the adsorption data follow both Langmuir and Freundlich isotherms. Fly ash mixed with calcium [195] for the Congo Red adsorption from solution with different initial concentration showed efficiencies as high as 93-98%.

- McKay et al. reported high adsorptive capacity of bagasse pith, resulted from the sugar cane industry without any pretreatment. They observed high values for the adsorption of basic dyes, 158 mg/g for Basic Blue 69 and 77 mg/g for Basic Red 22, while lower capacities of 23 mg/g and 22 mg/g were observed for Acid Red 114 and Acid Blue 25. Gupta et al. (2000) used bagasse fly ash for the removal of two basic dyes: rhodamine B and methylene blue. The bagasse pith was treated with hydrogen peroxide and then washed, dried and further sieved into desired particle sizes.
- Other studies shown that fly ash obtained from agriculture materials such rice husk ash [196] is a good adsorbent for acidic dyes removal. The optimum time for attaining equilibrium was found between 30-120 min. Also the authors suggested that ash can be used in suspension in batch processes or pelletized, which has technological advantages but involves new cost.
- Shale oil ash, an inorganic residue, obtained after the combustion of shale oil was used as adsorbent by Al Qodah [197] for dyes. The adsorbent materials which are obtained after a high temperature process, possesses good porosity and had good adsorption properties for organic and inorganic pollutants.

The adsorption capacity of raw fly ash is rather low but can be improved, usually by chemical treatment. Previous studies proved that conditioning by alkali treatment (1N - 3N) can be a viable path for enhancing the adsorption efficiency for removing heavy metals [209] or multi-component systems of heavy metals and dyes and/or surfactants [140]. The NaOH concentration used in these processes is significantly lower compared to the usually reported one of 5.6-8 N.

Alternative to adsorption, novel and efficient processes are under research as part of the tertiary treatment, mostly investigated being the Advanced Oxidation Processes.

Advanced Oxidation Processes (AOPs) rely on the generation of highly active hydroxyl free radicals, thus support almost universal oxidation.

Usually, as AOP are mentioned: photolysis (under UV irradiation), homogeneous photocatalysis (using Fenton systems and UV or VIS activation), heterogeneous photocatalysis (using wide band gap semiconductors, activated by UV or VIS radiation), and sonolysis.

Well optimized, AOP can oxidize organic pollutants to CO₂ and H₂O (mineralization).

Table 13. Summary of references on dyes adsorption on fly ash [83, 163]

Dye	Adsorbent (type)	Adsorption capacity [$\text{mg} \cdot \text{g}^{-1}$]	Adsorption isotherm	Kinetic model	References
Cristal violet	Fly ash (FA)	$9.76 \cdot 10^{-5}$	Freundlich > Langmuir	Lagergren First order	[193]
Basic Fuschin	Fly ash	$1.35 \cdot 10^{-5}$	Freundlich > Langmuir	Lagergren First order	[193]
Acid Red 1	Coal Fly ash (CFA)	92.59-103.09	Langmuir	Pseudo Second order	[198]
	CFA-600	32.79-52.63	Langmuir	Pseudo Second order	[198]
	CFA-NaOH (6N)	12.66-25.12	Langmuir	Pseudo Second order	[198]
Methylene Blue (MB)	Fly ash	$6.0 \cdot 10^{-6}$	Langmuir and Freundlich		[199]
	FA-HNO ₃	$2.2 \cdot 10^{-5}$	Redlich-Peterson		[200]
	FA-HNO ₃	$2.4 \cdot 10^{-5}$	Redlich-Peterson		[201]
	FA-NaOH	$8.0 \cdot 10^{-6}$	Langmuir and Freundlich		[199]
	FA	$2.0 \cdot 10^{-5}$	Langmuir	Pseudo Second order	[200]
	FA	5.718	Langmuir and Freundlich	Lagergren Fiest order Pseudo Second order	[202]
	FA - Columbian	$2.0 \cdot 10^{-5}$		Pseudo Second order	[203]
	FA - Thailand	$1.6 \cdot 10^{-6}$		Pseudo Second order	[204]
	FA	36.05	Langmuir	Pseudo Second order	[204]
	FA-NaOH	$8.0 \cdot 10^{-6}$	Langmuir and Freundlich		[205]
Malachite Green	FA	40.65	Langmuir	Pseudo Second order	
	Modified pine cone powder	129.87-142.25	Langmuir and Freundlich	Pseudo Second order	[206]
Rhodamine B	FA - Columbian	$8.0 \cdot 10^{-6}$		Pseudo Second order	[203]
	FA - Thailand	$2.5 \cdot 10^{-7}$		Pseudo Second order	[204]
Remazol Blue (RB)	Fly ash	75.1			[207]
Remazol Red (RR)	Fly ash	16.9			
Refection Yellow (RY)	Fly ash	26.6			
Reactive Orange li (RO16)	Zeolite-FA-iron oxide magnetic	1.06	Langmuir	Pseudo Second order	[208]
Indigo Carmine (IC)	Zeolite-FA-iron oxide magnetic	0.58	Langmuir	Pseudo Second order	

Regular oxidation and photolysis are implemented as:

- chemical oxidation using ozone;
- chemical oxidation combining ozone and hydrogen peroxide.
- Ultra-violet conjunction of H₂O₂ or Ozone (UV/H₂O₂; UV/O₃). In this case the dyes removal can be as high as 80%.

Homogeneous photocatalysis (Photo-Fenton process) combines the advantages of the regular Fenton mechanism with UV activation; the larger amount of hydroxyl radicals and the faster kinetic is efficient in removing a broad variety of dyes from wastewater [210]. The process efficiency depends on: solution pH, amount of H_2O_2 , Fe^{2+} dose, UV light intensity and the initial dye concentration.

Plenty of effort is now dedicated to *heterogeneous photocatalysis* [211], where the radiation energy excites an electron from the valence band of the catalyst to the conduction band with a series of reaction which results in the formation of hydroxyl radicals (by the interaction of holes with water molecules), able to oxidize most organic structures.

Various materials are reported as catalysts in dispersion or as thin films, such as oxides: TiO_2 , WO_3 , ZnO , SnO , ZrO , CeO_2 etc., or sulphides such as: CdS , ZnS etc. The process efficiency depends on several parameters: amount of catalyst, substrate surface or “concentration” and the dose of electron acceptors (H_2O_2), UV light intensity and the initial concentration of dyes in wastewater. Efficient heterogeneous photocatalysis has adsorption as first step; the working pH should be chosen as to promote electrostatic attraction between the dye and the substrate.

A study of the photocatalytic degradation of methyl orange (MO) and rhodamine 6 G (R6 G) employing heterogeneous photocatalytic process, and photocatalytic activity of various semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), stannic oxide (SnO_2), zinc sulfide (ZnS), cadmium sulfide (CdS), copper sulfide (CuS) have been carried out by Kansal et al. 2007, L. Isac et al. [211, 212]. The effect of process parameters versus the catalyst dose, dyes' concentrations and pH on the photocatalytic degradation of MO and R₆G was studied. Authors observed that irradiating the aqueous solutions of dyes containing photocatalysts with UV and solar light resulted in maximum decolourization (above 90%) with the photocatalytic system ZnO /solar light at alkaline pH or ZnO /UV system. The maximum adsorption of MO was noticed at pH = 4 with 1 g/L dose of catalyst, and of R₆G at pH = 10 with 0.5 g/L catalyst. Employing ZnO /solar light is better and the advantages are, besides the reduced costs, a smaller amount of sludge as a consequence of an increased COD removal.

In Table 14 are presented the activity of photocatalyst on different dyes used in textile industries.

Table 14. Reports on dyes photodegradation (selection)

Dye	Photocatalyst	Efficiency removal [%]	Observation	References
Methylene Blue (MB)	TiO ₂ - thin film	90.3	- glass coated TiO ₂ thin film - thin film illuminated by fluorescent lamps	[213]
Methyl Orange (MO)		98.5		
Indigo Carmine (IC)		92.4		
Chicago sky blue 6B (CSB)		60.3		
Mixed dyes (MB, MO, IC, CSB)		70.1		
Methlen Blue	Fe/ZnO/SiO ₂ Nanoparticles	95-100	Optimal conditions: - under visible light, pH = 4, illumination time is 30 min, the amount of catalyst loading is 0.075 g/L - C _i = 50 ppm MB dye solution	[214]
Malachite green (MG)	Bi ₂ WO ₆ - hydrothermally synthesized	98.9 30.63	- 98.9% under visible light, pH = 2, at after 30 min - 30.63% under visible light, pH = 8 - the relation between the rate of photocatalytic degradation and the concentration of malachite green can be described by the pseudo-first-order kinetics, rationalizing in terms of the Langmuir-Hinshelwood model	[215]
Methylene Blue	CdS, Cd _{0.98} Mn _{0.02} S, Cd _{0.96} Ni _{0.04} S Cd _{0.90} Cu _{0.10} S	91-98	- degradation efficiency in order: Cd _{0.90} Cu _{0.10} S > Cd _{0.96} Ni _{0.04} S > Cd _{0.98} Mn _{0.02} S ≈ CdS - under alkaline pH = 11.0 - irradiation time of 120 - kinetic behavior of photocatalytic reaction can be described by a modified Langmuir-Hinshelwood model	[216]
Safranin		86-95		
Methylene Blue	ZnO-SiO ₂ xerogel	99	- the economic point of view, 0.050 wt% is considered the best xerogel loading, after 40 min - 0.050 wt% of ZnO-SiO ₂ xerogel is enough for degradation about 99% after 40 min - kinetics of photodegradation of MB/ZnO-SiO ₂ photocatalyst was found to be of the first order	[214]
Methylene Blue	TiO ₂ -ZrO ₂	60	- after 6 h UV irradiation; - H ₂ O ₂ , optimize conditions increase the efficiency up 66.61%	[217]
Rhodamine B	ZnO- hydrothermally synthesized	66.94- 90.74	- pH = 6-7 - follows first-order kinetics - UV irradiation	[218]
Reactive Blue 49 (RB49)	Ag/ZnO- heterostructure nanocatalyst	90	- approximately 90-95% (RB 49)/Ag/ZnO, H ₂ O ₂ optimize conditions have been eliminated after 30 min. in the photocatalytic degradation rate of organic compounds is described by a pseudo first kinetic order, rate constant (K) is 0.57 min ⁻¹	[219]

As the data in the above table outlines, there are actually no reports on the use of fly ash-based composites with photocatalytic activity. This topic was for first time investigated - to the best of our knowledge - in our group.

Sonolysis, i.e., use of ultrasonic waves has been used for dyes bleaching. The mechanism proposed for the sonochemical processes is usually based on the formation of short-live radical species generated in violent cavitation events. The sonochemical degradation of dyes alizarin was studied by Hong et al. and Pankaj [220, 221] and the authors found the process to be dependent on ultrasound power and, total solution volume, and a decrease in the reaction rate was observed when changing the gas phase in the reactor from air to argon. It was suggested [222] that combining photocatalysis with sonication, enhanced dyes degradation is registered.

Other worker were oriented your researches for simultaneous technologies for removal dyes, heavy metals from wastewaters. This may be filtration with coagulation or coagulation with ozonation or coagulation with electrochemical oxidation and activated sludge for wastewater treatment textile wastewater. Adsorption and nanofiltration was applied for treatment of the textile dye house effluent containing a mixture of tow reactive dyes [223]. This means to combine the materials, one for adsorption and a membrane.

I.9. Conclusions, Limits and Solutions

The investigations on the state of the art outlined the following issues:

1. Although water is abundant on the Earth, humankind is facing a water crisis as result of the fast depletion of the water sources suitable and feasible for common use in household and economy.
2. Industrial wastewater is usually loaded with a broad range of pollutants and toxic substances. Among these, heavy metals and dyes represent to representative categories. Their removal is now-a-days done by conventional processes, designed to meet the threshold values set for discharge in the surface water flows.
3. For water re-use the threshold values are no longer enough and novel processes are required for advanced wastewater treatment. Market acceptable processes are based on low-cost materials and on low-energy consuming steps.
4. Two types of advanced wastewater treatment processes are promising candidates: adsorption and photocatalysis.
5. The use of wastes and natural compounds for advanced wastewater treatment represent a trend very much investigated, as meeting the pre-requisites of low-cost, high efficiency.
6. Fly ash - a waste produced in huge amounts in coal burning plants for thermal and electric energy production.
7. Fly ash composition is strongly depending on the coal type and source, the burning process and the burning reactor, thus there is a large variability in its surface properties.
8. Heavy metals removal on various types of fly ash are reported and optimized conditions depend on the fly ash surface. Most of the studies are related to single cation solutions and show that Langmuir and Freundlich isotherms are well describing the process.
9. The specific surface and charge of fly ash supports fast kinetics that may fall in one of the following categories: pseudo-first order kinetics, pseudo-second order kinetics and/or inter-particle diffusion
10. To reach a better control and reproducibility of the substrates, fly-ash based composites are reported with natural or artificial materials.
11. Fly ash also represents a suitable adsorbent for dyes, having the limitation of difficult desorption, thus of up-scaling.

12. The use of wide band gap semiconductors for dyes oxidation towards mineralization is well-known and represents a path for sustainable wastewater treatment.
13. Heterogeneous photocatalysis can be enhanced by combining with homogeneous photocatalysis (e.g. photo-Fenton systems).

These conclusions also outline the limitations of the current state of the art; the main limit is the separate approach of different advanced wastewater treatment processes, able to remove pollutants from different classes, as heavy metals and dyes are.

This significantly limits the up-scaling potential of these processes. The main limits and the needs related to lift the barriers are:

Limit 1: Up-scalable processes require low-cost adsorbents, able to be obtained in industrial sustainable processes. Current solutions based on ion exchangers have the main draw-back of a limited raw material-oil.

Required solutions: identify novel materials, based on natural abundant materials. A fully sustainable processes will use wastes as second raw materials for novel, efficient adsorbents. Fly ash represents such a solution. To tailor the fly ash properties and expand its potential in inorganics and organics adsorption, fly-ash based composites with photocatalysts would represent a novel, efficient material.

Limit 2: Industrial wastewaters are always loaded with more components (pollutant, toxic or benign) that are involved in concurrent processes when subjected to adsorption or photocatalysis.

Required solution: identify substrates able to face concurrent adsorption/photocatalysis or substrates that can be activated after the fast adsorption of one component.

Limit 3: Sequential adsorption and photocatalysis requires complex industrial reactors/columns/ reactors and accurate control.

Required solution: identify simple processes, if possible single-step processes combining adsorption and photocatalysis.

I.10. Aim and Objectives of the Research

Based on this analysis, a research plan was formulated. The aim and the specific objectives are:

Aim: To develop novel adsorbent materials, based on fly ash for advanced simultaneous removal of inorganic and organic pollutants in processes based on adsorption and photocatalysis.

Specific objectives:

- O1. To develop novel efficient substrates, fly-ash based for inorganic and organic pollutants removal from industrial wastewaters.
- O2. To synthesize and optimize complex adsorbent/photocataysts systems, fly ash-based for the simultaneous removal of inorganic and organic pollutants from industrial wastewaters.
- O3. To develop and optimize advanced wastewater treatment up-scalable processes, based on fly ash adsorbents.

II. Design of Experiments

Based on the objectives set for the research, the experimental plan was based on the concept of novel materials development; optimization was done considering the main output property, the efficiency in the pollutant(s) removal.

Additionally, aspects related to the fundamentals of the investigated processes are detailed based on the studies of the isotherms and kinetic mechanisms.

The experimental activities were developed in the R&D Center Renewable Energy systems and Recycling, in the Transilvania University of Brasov, Romania.

The experimental plan was developed in three steps:

I. Novel fly ash based substrates, efficient in heavy metals or dyes adsorption

1. Conditioning the fly ash surface, for enhancing the efficiency and the reproducibility.
2. Developing fly ash based composites with natural abundant materials (bentonite, diatomite), for enlarging the range of pollutants that can be removed.
3. Developing fly ash based composites with common adsorbents (activated carbon).
4. Developing fly ash based composites with photocatalysts as a first step towards simultaneous removal of heavy metals and dyes via adsorption and photocatalysis.

II. Novel fly ash based substrates for combined processes of photocatalysis and adsorption for organic and inorganic pollutants simultaneous removal

1. Comparative investigation of adsorption (dark) and photocatalysis in multi-pollutant wastewater treatment.
2. Optimization of the simultaneous removal of heavy metals and dyes in adsorption and photocatalysis.

III. Novel zeolite-type materials for the advanced wastewater treatment with complex pollutant load

1. Developing zeolite-type materials through mild hydrothermal synthesis of fly ash.

2. Optimisation of the advanced treatment of wastewaters with complex pollutants load using zeolite-type materials.

Equipment

Conditioning and synthesis:

- Fly ash conditioning was done in batch processes, under stirring, at room temperature.
- The zeolite-type materials were synthesized in an autoclave, with temperature and pressure control Hel Limited UK model.

Materials characterization:

1. *Crystallinity and polymorphism* were investigated using an Advanced D8 Discover Bruker Diffractometer, $\text{Cu}_{K\alpha 1} = 1.5406 \text{ \AA}$, 40 kW, 20 mA, 2θ range $10^\circ \dots 70^\circ \dots 80^\circ$, scanning step 0.02° , scan speed 2 sec/step.
2. *Inter- and intra-bonds* were investigated using FTIR spectroscopy (Spectrum BX Perkin Elmer BX II 75548, $\lambda = 400\text{-}4000 \text{ nm}$).
3. *Morphology, topology and macro-porosity* were investigated using: AFM (Ntegra Spectra, NT-MDT model BL222RNTE, in semi-contact mode with Golden silicon cantilever, NCSG10, at constant force 0.15 N/m, with a 10 nm tip radius) and SEM (S-3400N - Hitachi, accelerating voltage of 20 KV) equipped with EDS for surface elemental composition (dispersive X-ray spectroscopy, EDS, Thermo Scientific Ultra Dry).
4. *BET surface and micro-porosity* was investigated using Autosorb-IQ-MP, Quantachrome Instruments.
5. *Surface energy* was evaluated based on contact angle measurements using the sessile drop method (OCA-20 Contact Angle-meter, Data Physics Instruments).

Pollutants analyses:

1. Heavy metals decay was investigated using atomic spectroscopy (AAS Analytic Jena, ZEE nit 700), at the characteristic wavelength of each heavy metal (specific lamp source).
2. Dyes and cationic surfactants were investigated using UV-VIS spectroscopy, in the range of 200-900 nm (Perkin Elmer Lambda 950 UV/VIS) at the maximum absorption wavelength of each component.

III. Fly Ash - Based Substrates for Advanced Wastewater Treatment

III.1. Conditioning the Fly Ash - Based Substrates [224, 225, 226, 227, 228]

In the past century the living standard has risen along with an increased demand for energy. Large amounts of energy are obtained from coal in Combined Heat and Power (CHP) Plants obtaining a large amount of the coal combustion products (CCP): fly ash, bottom ash, boiler slag and flue gas desulphurization materials. According ACAA, the weight percentage of ash to coal buried world-wide is almost 10-15 wt% out of which 10% is bottom ash and the rest is fly ash (FA). Thus, FA recycling represents a priority, today.

Fly ash represents a waste which raises huge environmental concerns. Although industrial reuse is already implemented, the FA amounts are much larger; therefore novel recycling solutions are continuously searched for. During the past five years over 7000 papers were indexed in ISI Thompson Web of Science, dealing with this topic, among which, over 1400 were published in 2012-2013. This proves that the use of FA as second raw material is a highly investigated topic, not solved yet. This is the case also for other wastes used as second raw materials; therefore, developing a complex study that includes also the development of an algorithm for optimizing the synthesis process of novel materials based on second raw materials is expected to bring knowledge that can be transferred within the advanced materials research and represents an approach that is not fully valorised yet.

Considering its generic composition, FA can also be used as a low-cost adsorbent, solving two major environmental problems, by recycling and reducing the air and water pollution and by developing novel products. A more recent approach is to use FA as a resource for advanced adsorbent materials used for heavy metals (HM: cadmium, cooper, nickel, iron, lead, zinc) and dyes (methylen blue - MB, and methyl orange - MO) [224, 225, 226, 227] removal.

The fly ash surface properties are strongly depending on many factors, including the coal type/composition, the coal- burning process in the power plant and the furnace characteristics. The differences are related to the oxides and carbon composition in the fly ash and recent

studies proved that the heavy metal adsorption effectiveness is enhanced by the CaO content [228, 229, 230]. These differences are registered even at the same CHP, from one coal batch to another and raise significant problems when designing a technology aiming at fly ash reuse as novel adsorbent. Therefore, fly ash should be conditioned, for getting a more constant (and reproducible) composition. Obviously, the conditioning process will also target the enhancement of the surface properties, by increasing the amount and affinity of the active sites, for a given group of pollutants.

Conditioning aims at accelerated solubilisation of chemically unstable or water-soluble compounds, followed by re-precipitation of low solubility compounds; the development of higher BET specific surfaces represents a complementary aim, along with the control of the surface charge (value and sign). For the removal of heavy metals cations, the surface should be negatively charged, while for organics removal, the charge is depending on the predominant charge of the pollutant.

The use of concentrated NaOH solutions for modifying the FA surface is reported, in processes at room temperature [156], and in hydrothermal processes [231]. The chemical reactions on the FA grains surface are complex leading to composition modifications, due to dissolution and precipitation of various compounds, mainly alumina-silicates [156] and rearrangements of the oxide/carbon phases in the FA; crystalline modifications can also appear, increasing the amorphous phase; this treatment can lead (at extreme pH and temperature) to the development of ion exchanging surfaces, of zeolite type [231]. But, the use of highly concentrated NaOH solutions (8M [231], or pH = 13.95 [232]) can rise environmental problems and increases the complexity of the wastewater treatment technology. Therefore, alternatives must develop: either the use of less concentrated NaOH (0.5N, 1N, 2N, even 4N) solutions for surface modification and/or the use of other surface modifiers.

Heavy metals are easily reacting with chelating agents such as Complexone III (the sodium salt of the ethylenediamine tetraacetic acid) solution (CIII, Rearal, 99%, c = 10%), Eriochrome Blacke T solution (EBT, 96%, c = 0.5%) or Pyrocatechol Violet solution (PV, Merck, 98%, c = 0.5%) [228].

Following this rational, FA surface was modified, by batch mixing for 48 hours, of a 1/10 ratio dispersion of FA with each chemical agents. The first experiments used FA collected

from the electro-filters of the CHP Brasov plant (FA-CET), with the composition presented in Table 15 [228].

Table 15. *The composition of fly ash - CET Brasov, [%]*

Compound	Fly Ash ELF	Fly Ash and Cinder	Compound	Fly Ash ELF	Fly Ash and Cinder
SiO ₂	53.32	52.84	Fe ₂ O ₃	8.97	8.58
Al ₂ O ₃	22.05	22.14	MnO	0.08	0.08
Ca O	5.24	4.58	TiO ₂	1.07	1.17
MgO	2.44	2.40	SO ₃	1.40	0.88
K ₂ O	2.66	2.68	P ₂ O ₅	0.12	0.13
Na ₂ O	0.63	0.72	LOI*	1.58	3.42

*LOI: loss of ignition (corresponding to organics)

The XRD peaks in Fig. 16 prove a complex composition, rich in various inorganic components (oxides and salts); graphite is also present in the FA, in almost constant amount in the unmodified and in the modified FA. The data also show crystalline modifications up to 36.83% that can be attributed to dissolution of tetragonal (t) SiO₂ followed by re-precipitation of orthorhombic (o) SiO₂ forming aggregated particles with diameters less than 5 μm; these develop fractured morphologies, with more edges, consequently a surface with higher roughness, as presented in Fig. 17.

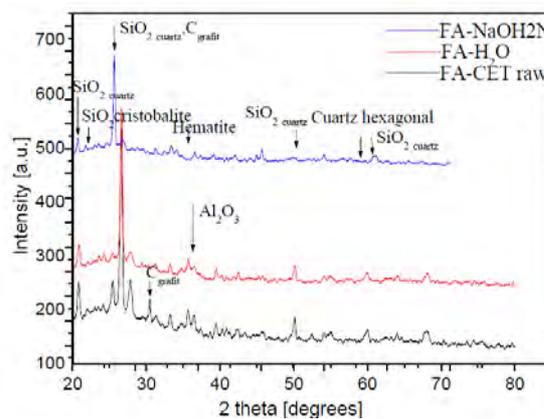
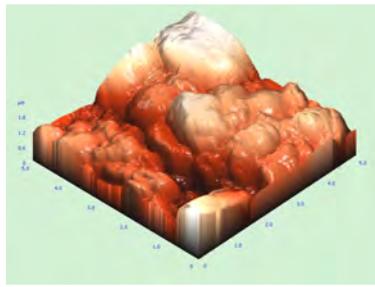
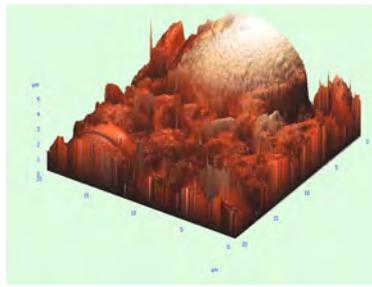


Fig. 16. *XRD patterns of FA raw, washed and treated with NaOH 2N*

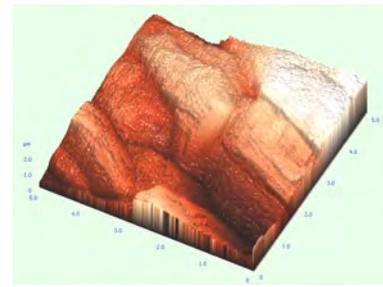
The surface morphology is changed, Fig. 17c, d. The raw FA consists of conglomerates of spherical particles, with diameters ranging from 1 to 30 μm. The FA modified with NaOH 2N leads to higher specific surface and increased dimension homogeneity that can explain the high efficiencies registered in heavy metals removal even at very short contact times.



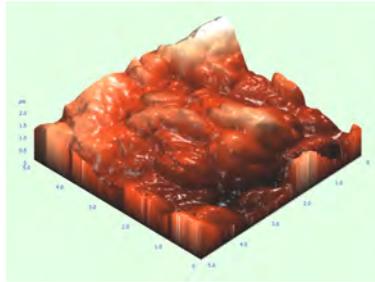
a) FA-CET raw
Average roughness: 300 nm



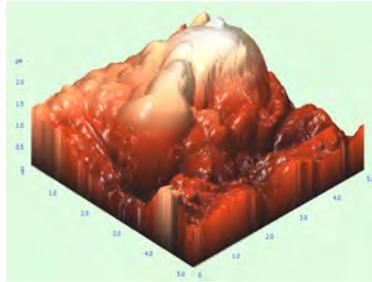
b) FA-CET washed
Average roughness: 431.3 nm



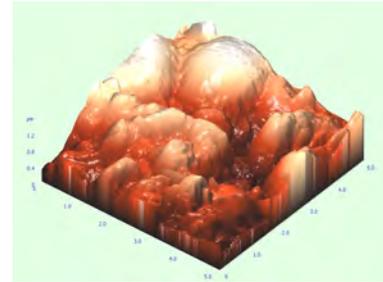
c) FA-CET treated, HCl 2N
Average roughness: 361.8 nm



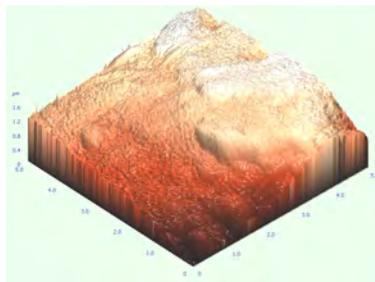
d) FA-CET treated, NaOH 1N
Average roughness: 314.3 nm



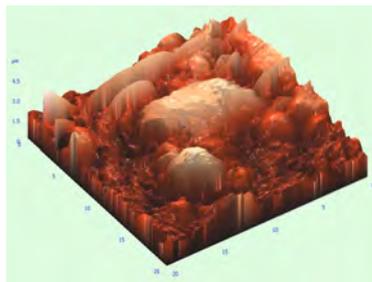
e) FA-CET treated, NaOH 2N
Average roughness: 93.4 nm



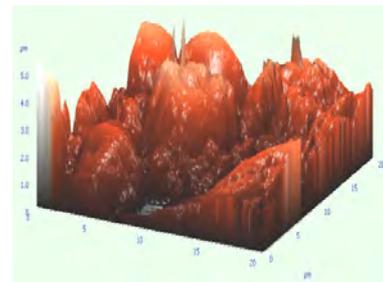
f) FA-CET treated, NaOH 4N
Average roughness: 254.4 nm



g) FA-CET/Complexone III 0.25M
Average roughness: 280.9 nm



h) FACET/Pyrocatechol Violet 0.5%
Average roughness: 632.1 nm



i) FA-CET/Eriocrom Blacke T 0.5%
Average roughness: 671.4 nm

Fig. 17. Surface morphology of: a) raw FA; b) washed FA; c) FA modified with HCl 2N; d) FA modified with NaOH 1N; e) FA modified with NaOH 2N; f) FA modified with NaOH 4N; g) FA modified with CIII; h) FA modified with PV; i) FA modified with EBT [228]

III.2. Optimizing the Fly Ash Based Substrates for Heavy Metals Removal

[227, 228, 233]

To test the efficiency of these substrates, the experimental protocol was designed for heavy metals removal via adsorption.

The experiments were conducted, under mechanical stirring, at room temperature using cadmium and nickel ions from aqueous solutions in a broad concentration range: 10-1000 mg/L. These two cations were chosen because: (i) cadmium is one of the most toxic cations, quite pH sensitive (at $\text{pH} > 8.1$ it forms the insoluble cadmium hydroxide); (ii) copper is another heavy metal but with lower toxicity, still having a low discharge limit (ii) in water both cations are hydrated as $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{H}_2\text{O})_{4...6}]^{2+}$, thus they have different volume, different mobility and are expected to well test the adsorption limits of the substrates.

Heavy metal concentrations, before and after adsorption were evaluated by atomic adsorption spectroscopy (AAS) (Analytic Jena, ZEE nit 700), at $\lambda_{\text{Cd}} = 228.8$ nm, at $\lambda_{\text{Ni}} = 232.0$ nm and $\lambda_{\text{Cu}} = 324.75$ nm.

The adsorption efficiency, η , and capacity q_t were evaluated based on the optimal time and mass balance previously set:

$$\eta = \frac{(c_{HM}^i - c_{HM}^t) \times 100}{c_{HM}^i},$$

$$q_t = \frac{(c_{HM}^i - c_{HM}^t) \times V}{m_{ss}},$$

where c_{HM}^i and c_{HM}^t represent the initial and momentary equilibrium concentrations of the heavy metal (HM, mg/L), V the solution volume (L) and m_{ss} is the amount of solide substrate (g).

The immobilization efficiency of Cd^{2+} and Ni^{2+} from mono-cation solution metal are discussed in connection with contact time from 5 min up to 60 min., wastewater volume: adsorbent mass ratio (1 g : 100 mL) and ions concentration; Langmuir and Freundlich mechanisms were found to describe the adsorption processes. The process follows a pseudo-

second order kinetic, for both metals, on the entire concentration range. Highly efficient adsorption, even at very low heavy metals concentrations (20 ppm), is registered for fly ash modified with NaOH.

As expected considering their mobility, copper cations adsorb faster and with higher efficiency. Therefore, further investigations focused on cadmium cation adsorption.

As reference, adsorption tests were done on wet activated carbon powder (Merck), to evaluate the contribution of the carbon content in FA on the cadmium removal efficiency. The results proved that the carbon, even activated does not represent the major constituent in the very good FA efficiency.

Further modified FA substrates are tested, targeting the increase in the cadmium adsorption efficiency, Fig. 18.

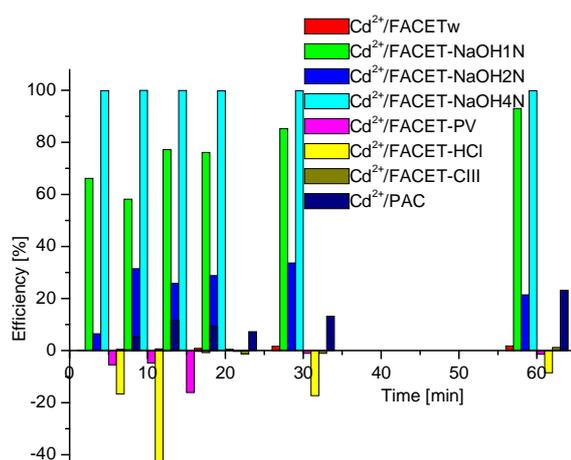


Fig. 18. The removal efficiencies of Cd^{2+} ions from aqueous solutions on FA-modified substrates [228]

The results showed that the lowest heavy metals adsorption efficiency occurred when the FA was treated with HCl 2N, this effect being caused by a positive surface charge leading to repulsions between the surface ($\equiv SiOH_2^+$) and metal ions. Similar poor efficiencies are registered when using complexation agents (CIII, PV) as FA modifiers and the desorption registered on FA modified with PV (Fig. 18) could be the result of the development of very smooth morphologies. By using EBT as modifier the removal efficiencies are good (as result of selective dissolution, responsible for high specific surface morphologies), Fig. 17i. Still, the use of EBT is limited by the costs.

The cadmium adsorption efficiency on FA modified with NaOH of different concentrations proves that different reactions are developed at different concentrations (1N, 2N and 4N)

which may increase the adsorption capacity of substrate, Fig. 19.

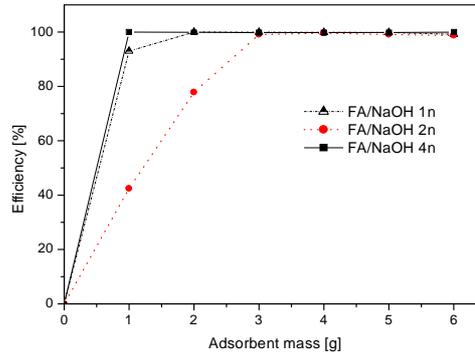


Fig. 19. Cadmium immobilization efficiency vs. substrate weight

Similar adsorption experiments were further developed for more heavy metals cations: Ni²⁺, Cu²⁺. Adsorption efficiency at various contact time, up to 60 min, are presented in Table 16, both for cadmium and nickel on washed and modified FA with NaOH 2N.

Table 16. Adsorption efficiency, [%], of the Cd²⁺ and Ni²⁺ ions on FA*

Time [min]	FAw		FA modified with NaOH 2N	
	Cd ²⁺	Ni ²⁺	Cd ²⁺	Ni ²⁺
10	0.5	10.11	31.47	99.88
20	0.87	10.24	25.85	99.95
30	1.65	10.33	33.67	99.87
60	1.78	10.58	21.48	99.85

* 1 g substrate/100 mL solution; c_{ion} = 0.01N.

Nickel is removed from aqueous solutions using FA washed and FA modified with NaOH 2N, with efficiencies above 99%. The higher maximum adsorption efficiency for nickel can be related with its ionic volume and the partial loss of hydration water, which runs differently for cadmium and nickel at the natural pH of the cations solutions.

The optimized adsorption conditions are presented in Table 17.

Table 17. Optimized adsorption conditions on FA modified with NaOH

Optimized parameter	Cd ²⁺			Ni ²⁺
	FA/NaOH 1N	FA/NaOH 2N	FA/NaOH 4N	FA/NaOH 2N
Contact time	60 min	30 min	10 min	20 min
Adsorbent mass: 100 mL solution	2 g	4 g	1 g	3 g

Adsorption experiments were developed for concentrations covering the extreme values that can be registered in the wastewater treatment from the electroplating industry. In the optimized conditions, the adsorption of both cadmium and nickel ions is efficient on a broad concentration range (Table 18):

Table 18. Cadmium and nickel adsorption efficiencies in the optimized conditions

C_{Ca} [ppm]	Efficiency [%]			C_{Ni} [ppm]	Efficiency [%]
	FA/NaOH 1N	FA/NaOH 2N	FA/NaOH 4N		FA/NaOH 2N
21.66	98.59	97.41	95.61	13.35	98.92
47.48	98.26	98.44	87.65	35.78	98.94
146.62	99.70	99.50	96.28	52.08	99.93
432.16	99.95	99.82	96.95	102.1	99.76
935.5	99.97	99.45	99.96	220.16	99.88

Although the most convenient adsorption conditions are registered for FA-CET/NaOH 4N, from a technological point of view, less concentrate alkaline solutions are desired. Efficiencies above 95% were obtained on FA modified with NaOH 4N after 5 min of contact while efficiencies of about 35% were obtained using FA modified with NaOH 2N, after 30 min., which is technologically feasible in a dynamic wastewater treatment process [233]. However, the use of NaOH 4N raises supplementary environmental problems and complicates the up-scaled process; therefore further studies were done for increasing the adsorption efficiency on FA modified with NaOH 2N by optimizing the ratio adsorbent mass: solution volume.

The cations adsorption efficiency strongly increases when the adsorption substrate is FA washed with NaOH 2N. We can conclude that the predominant process on the FACET-NaOH 2N surface is the heavy metal adsorption, with very good results for nickel and copper cation, Fig. 20.

The experimental data were used for identifying the adsorption mechanisms.

The Langmuir model describes the absorption of both metals and the linearization (analogue of the Scatchard plot [234], was well fitted, Fig. 20; this confirms the preferential adsorption of the heavy metal cations on the oxide FA CET-NaOH surface.

The adsorption of nickel ions on FA-CET modified with NaOH 2N solution is well modelled both by the Freundlich isotherm and Langmuir model for all the concentrations between 10-250 ppm. The high value of Freundlich k parameter (10.2) show that the nickel ions had developed strong bonds with the active adsorptions centres, most likely as chemo-sorption.

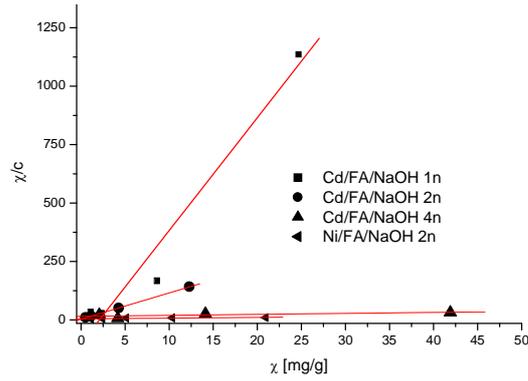


Fig. 20. Linearization of the Langmuir isotherm [228]

The Freundlich isotherm could not be fitted for cadmium on the entire concentration range.

In the optimized conditions, cadmium removal efficiencies are higher than 99%, for medium and large concentrations. For low concentration, when diffusion becomes significant, the overall efficiencies are lower and re-circulation is needed in order to comply with the discharge regulations.

Table 19. Adsorption efficiency of cadmium and nickel cations on FA-CET/NaOH 2N

Concentration [mg/L]	Cd ²⁺	Ni ²⁺
Below 50	97.92	99.93
50...100	98.87	99.93
100...200	99.50	99.76
Over 200	99.63	99.88
Discharge concentration [mg/L]	0.2	0.5

The adsorption kinetics gives information on the rate of heavy metal uptake, on the adsorbent surface and supports tailoring the adsorbent surface for the target, in this case - cadmium and nickel adsorption on FA-CET/NaOH 2N (1 g/100 mL) from aqueous solutions.

Three kinetic mechanisms are usually reported for adsorption on heterogenous substrates as is the fly ash: pseudo-first order, pseudo-second order and interparticle diffusion, expressed by Eqs. (38) - (40) [158, 159, 161]:

$$\log(q_e - q) = \log(q_e) - \frac{k_1}{2.303} t, \tag{38}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \tag{39}$$

$$q = k_{id} t^{1/2} + C, \tag{40}$$

where q and q_e represent the amount of metal adsorbed at the moment (t) and at equilibrium (mg/g), and k are the reaction rates.

Based on the correlation calculations, it could be proved that only the pseudo-second order kinetic can describe the process, with correlation factors, R^2 , above 0.930, as presented in Table 20 and Fig. 21 for (a) cadmium and (b) nickel.

Table 20. The parameters of the pseudo-second order kinetic for Cd^{2+} and Ni^{2+} adsorption on FA/NaOH 2N

Ion	k_2 [g/mg min]	q_e [mg/g]	R^2
Cd^{2+}	0.008	29.58	0.937
Ni^{2+}	4.122	22.03	1.00

This mechanism confirms that the active sites *and* the metal ion concentration are of equal importance. The higher maximum adsorption capacity for nickel can be related with its ionic volume and the partial loss of hydration water, which runs differently for cadmium and nickel at the natural pH of the test solutions.

A compromise should be reached between the contact time and the amount of substrate in a given volume of pollutant solutions, when targeting the use of the FA substrate modified with NaOH 2N. Therefore, new series of tests were done by adding only 2 g of substrate to 100 mL solution of Cd^{2+} , 0...400 mg/L ($CdCl_2$, Scharlau Chemie) and Cu^{2+} , 0...400 mg/L ($CuCl_2$, Scharlau Chemie). The mixture was stirred up to 90 min at room temperature, then the substrate was removed by vacuum filtration and the supernatant was analyzed. The results are presented in Fig. 21, show good removal efficiencies, both for cadmium and copper.

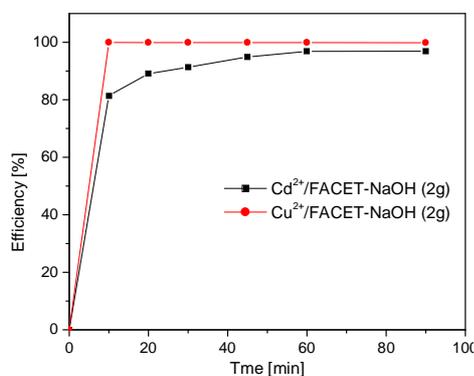


Fig. 21. Adsorption efficiency vs. contact time: a) Cd^{2+} ; b) Cu^{2+}

III.3. The Influence of the Fly Ash Source on the Heavy Metals Adsorption Efficiency [225, 228, 235, 239]

As already outlined, the FA composition depends on the coal source and burning parameters. To investigate the importance of the FA source, comparative studies need to be done, using FA from different sources.

Two types of raw FA were collected from the electro-filters of two CPH plants, from Brasov (FA1) and from Mintia (FA2), Romania. The sum of the SiO_2 , Al_2O_3 and Fe_2O_3 is, for both ashes, above 70% therefore, according to the ASTM standards, both FA are of type F. Consequently, ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the FA is mainly responsible for the substrate efficiency and the grains are not aggregating, even during long contact with water.

The ash was washed in ultrapure water, by stirring (50 rpm), at room temperature, for 48 h, to remove the soluble compounds. The main characteristics of the two FAs are presented in Table 21.

Table 21. Fly ash characterization

Ash	FA Composition [%]										pH*	κ^* [μS]
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	LOI		
FA1	53.70	21.60	9.56	3.63	2.39	2.20	0.68	0.76	0.05	3.80	10.45	0.4
FA2	46.05	20.08	9.93	6.07	2.35	2.28	0.83	0.06	0.09	4.45	11.48	0.4

* Measured after 48 h stirring of FA (4 g) in ultrapure water (100 mL).

Modified fly ashes: After washing and drying, samples of FA1 and FA2 were stirred, for 48 h, in NaOH 2N alkaline solutions. Afterwards, the dried modified FAs were washed in ultrapure water, until constant pH (FA1: 10.55 and FA2: 11.69) then dried again at 120 °C for 2 h. The substrates are further nominated as FA1/NaOH 2N and, respectively, FA2/NaOH 2N.

The solution resulted after washing FA1 and FA2 with water proved an ionic content (rather high conductivity) as result of the soluble compounds dissolution. The sodium and potassium compounds (largely oxides) are mainly responsible for the alkaline pH values, but also cadmium was found in the waters. The soluble cadmium content amounts 0.348 mg/L in the washing-water from FA1 and 0.059 mg/L for FA2. In EU, most national discharge regulation admit a maximum Cd^{2+} concentration of 0.3 mg/L thus, washing FA prior using is a compulsory step.

The XRD pattern of FA1 and FA2 washed and treated with NaOH 2N are presented in Fig. 22.

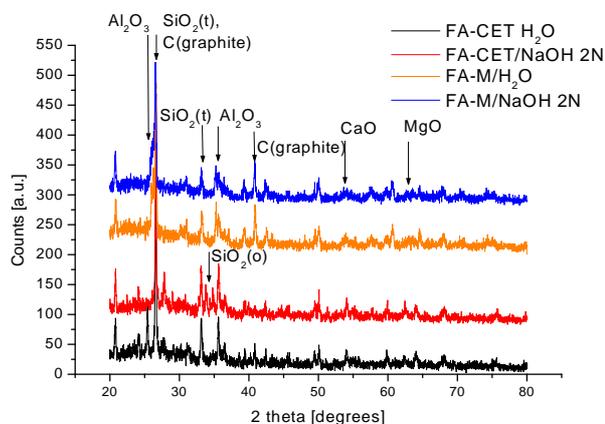
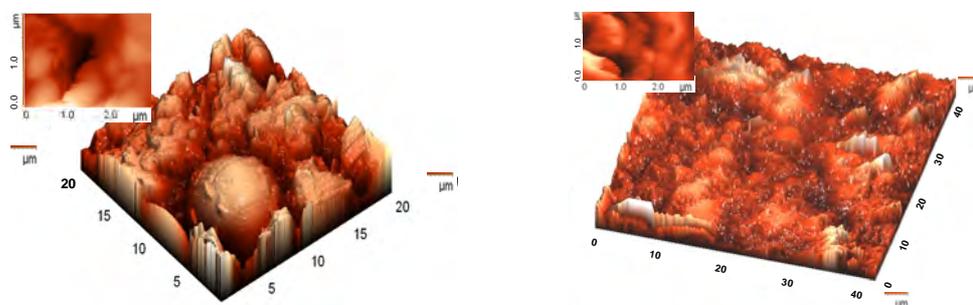


Fig. 22. XRD patterns of washed and treated FA [235]

The results show that certain components are less affected by NaOH during the reaction conditions, as there are CaO and unburned carbon (LOI - loss of ignition). Dissolution, enhancing the specific surface, affects Al₂O₃, MgO and, partially, SiO₂. On FA1, the tetragonal silica dissolution followed by the re-precipitation of the orthorhombic polymorph can be a supplementary cause in increasing the adsorption efficiency.



a) Average roughness: 485 nm

b) Average roughness: 393 nm

Fig. 23. FA1 (a) and FA2 (b) washed with water and modified with NaOH 2N

The AFM images, presented in Fig. 23a and b support these observations. During the contact with NaOH solution, the micro-structured ash conglomerates are developing aggregates with large open pores, accessible to the hydrated cadmium ions.

Even after a long contact (48 h) with NaOH 2N, there is not a unique surface aspect for both FA types; the morphology changes must be correlated with the surface reactions during modification: (re)precipitations lead to fractured surfaces (FA1), while predominant

dissolution is likely to leave smoother surfaces (FA2). Further adsorption is expected on high energy sites, mainly on edges. The dissolution processes can be considered as predominant and with stronger influence on the adsorption capacity which is almost equal for both substrates.

Adsorption experiments on the washed FA showed null efficiency in cadmium removal. Therefore, activating the surface represents a logical step. Previous studies [235], proved that an optimum surface charge is obtained by using NaOH 2N as modifier. The dynamic adsorption results, using 1 g FA in 100 mL cadmium solution with an average initial concentration of 700 mg/L are presented in Fig. 24, compared with the results obtained using TiO_2 as adsorbent. Influence of adsorbent mass for both substrates are presented in Fig. 24.

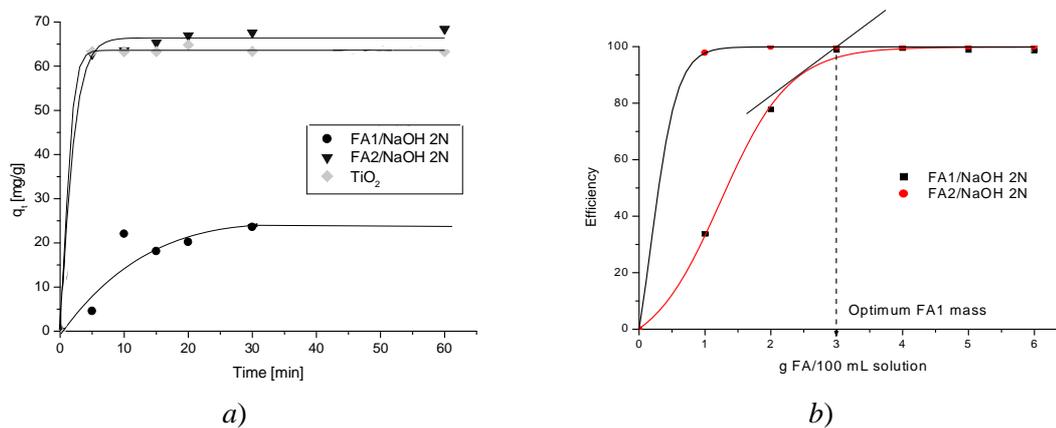


Fig. 24. a) Comparative dynamic adsorption studies of Cd^{2+} on modified FA and TiO_2 ; b) Adsorption efficiency on modified FA. Influence of adsorbent mass

As the results show, equilibrium is reached within maximum 30 min for all the substrates. From a technological point of view, in a dynamic wastewater treatment process, a 30 min flow period in the reactor is feasible; therefore further studies were done for optimizing the process to reach high efficiencies within this time. To increase the cadmium removal efficiency, test were done to optimize the ratio adsorbent mass: solution volume. The results, presented in Fig. 25, show an optimum ratio of 3:100 g/mL.

Experiments were done to test the adsorption efficiencies of heavy metals on the FA1 and FA2 substrates and the results show a good adsorption capacity of FA2NaOH 2N in removing Cd^{2+} , Cu^{2+} or Ni^{2+} from mono-cation solutions, Figure 26.

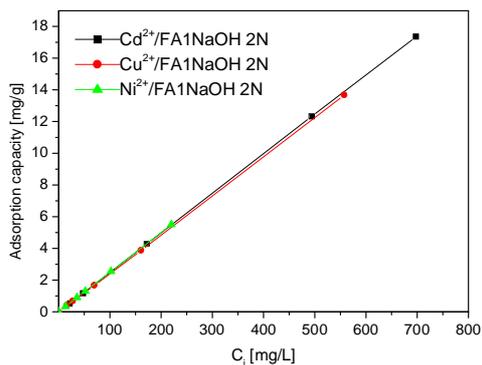


Fig. 25. Adsorption capacity of Cd^{2+} , Cu^{2+} , Ni^{2+} on modified FACET (FA1NaOH 2N)

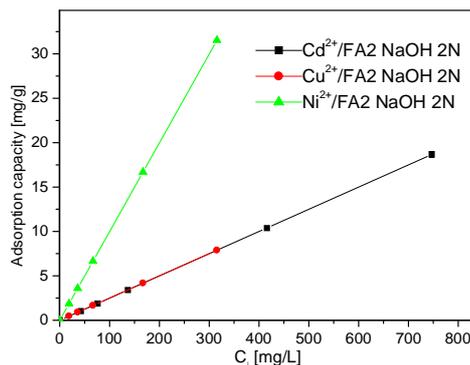
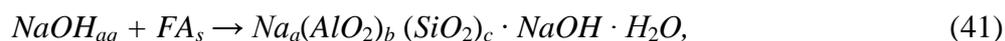


Fig. 26. Adsorption capacity of Cd^{2+} , Cu^{2+} , Ni^{2+} on modified FAM (FA2NaOH 2N)

The results prove that the conditioning processes are different, and are mainly influenced by the silica and alumina content; during alkali conditioning with NaOH 2N for 48 h, several interactions are expected, according to the following reaction [236]:



when on the FA surface can developed new active site ($\equiv SiO^-$) and ($\equiv AlO^-$) which allows metals to form complexes at the surface (Eq. 42, 43) [237, 238, 239]:



These reactions are different, depending on the type of FA. By dissolution of acidic oxides, the specific surface area is enhanced and activated and the efficiency of heavy metals removal increases. The re-precipitation processes can lead to new polymorphs and provide a large specific surface, suitable for adsorption.

III.4. Alternatives in Conditioning the Fly Ash Substrate [224, 226, 239]

Previous studies proved that further conditioning washed FA by alkali treatment (FA/NaOH 2N) is needed for enhancing the adsorption efficiency of heavy metals or multi-component systems of heavy metals and dyes [225], on fly ash.

As a separate group of studies showed, dyes also well adsorb on FA, thus they can also act as conditioning compounds. The expected advantage is the development of a uniform mono-layer, with predictable charge, that can be tailored according to the pollutant that should be removed.

Therefore, a new set of samples were prepared using washed FA further treated with methyl orange, Merck 0.01%, under 48 h stirring followed by filtration; this substrate was treated with NaOH 2N under 48 h stirring (FA/MO/NaOH 2N) - to get the required negative charge for cations adsorption, followed by filtration, washing with ultra pure water and drying, at 105-120 °C for 2 h.

The XRD spectra, Fig. 27, show that the major components of FA/MO/NaOH 2N are: carbon, SiO₂ in various structures (cubic, rhombohedral) and combined with Al₂O₃ as silimanite (Al₂SiO₅), mullite (3 Al₂O₃ · 2 SiO₅), along with γ -Al₂O₃, hematite (Fe₂O₃) and CaO.

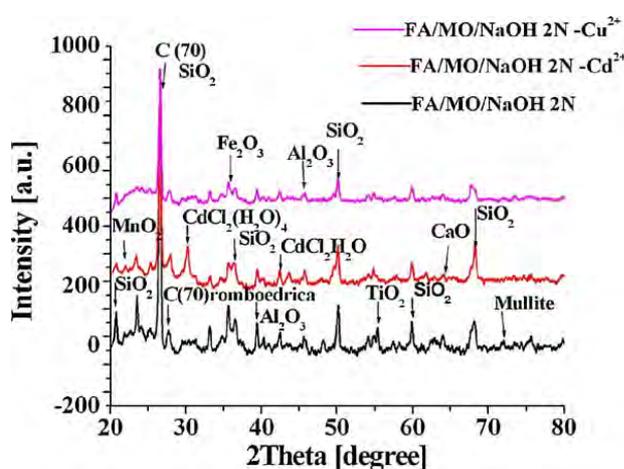


Fig. 27. XRD patterns of FA/MO/NaOH 2N before and after heavy metals adsorption [224]

After cadmium and copper cations adsorption, these compounds could be identified in crystalline compounds, in the surface, confirming that adsorption is likely to be the result of chemical modifying reactions, although without preferential dissolution of the major components.

These chemical and structural changes also induce surface morphology modifications, resulting in significant differences in the substrates' affinity for Cd^{2+} and Cu^{2+} before and after treating with NaOH 2N and MO 0.01% (Fig. 28).

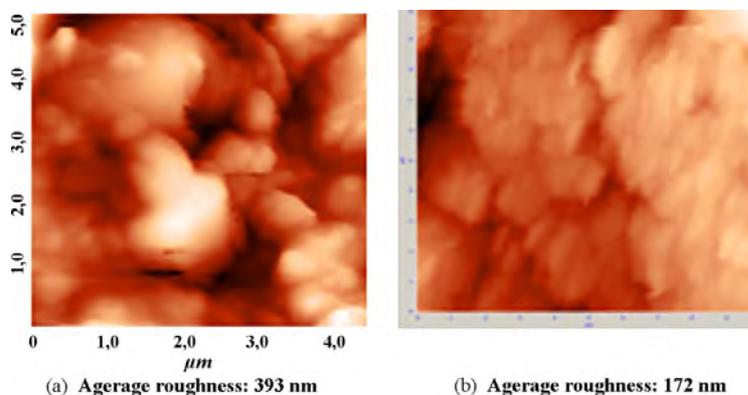


Fig. 28. FA morphology before and after treatment [224]

The average roughness significantly varies and can be explained by the dissolution/re-precipitation processes of alkaline oxides (confirmed by the high conductivity and TDS values) after treatment, leading to a surface with more uniform aspect that facilitates single mechanisms adsorptions process.

The variations in the adsorption efficiency for a 1:100 ratio FA/MO/NaOH 2N: metal solution volume is presented in Fig. 29.

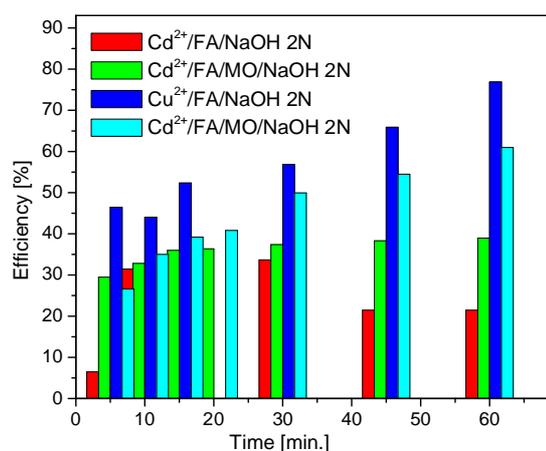


Fig. 29. Heavy metals adsorption efficiency on modified FA: Cd^{2+} and Cu^{2+}

The results allow setting the optimal contact time at 30 min, a value considered technologically feasible for both substrates and cations. The effect of the adsorbent mass on

the adsorption efficiency was investigated; it was proved that good Cd^{2+} adsorption occurs at a dose of 4 g FA for 100 mL solution. The optimized adsorption process for cadmium was then applied for solutions containing copper.

A similar path was followed for optimizing the conditions for Pb^{2+} and Zn^{2+} adsorption from synthetic aqueous solutions. Fly ash was modified in two steps: (1) with *NaOH 2N solution followed by (2) a treatment in methyl orange 0.2 mM solution, FA-NaOH-MO* [239]. The dried FA-NaOH was sieved and the 40-100 μm fractions were selected for adsorption experiments.

Parallel investigations were conducted on FA modified only through alkali treatment and on the FA-NaOH-MO substrate.

Both substrates were characterized using XRD for FA crystalline structure and AFM images (for morphology studies (roughness surface, pore size distribution)).

The XRD spectra, Fig. 30, show that aluminium silicate and other oxide components vary from one type of substrate to another supporting the assumption of surface modifications.

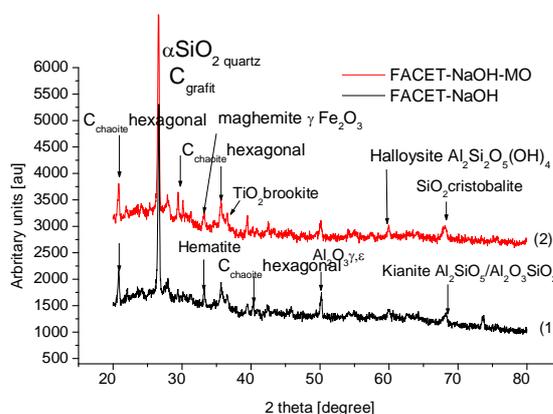


Fig. 30. XRD of FA modified with: *NaOH 2N*, (1); *NaOH 2N and MO 0.02 Mm*, (2) [239]

Methyl orange molecule, with two aromatic rings can act as an electron donor in the interaction with the heavy metals cations, Fig. 31.

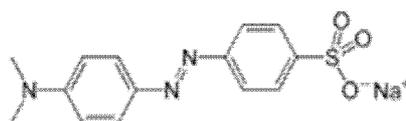


Fig. 31. Chemical structure of Methyl orange in alkali solution

Therefore, the alkali form of MO may act as a supplementary complexing agent, which, adsorbed on the FA surface can increase the affinity for heavy metals by the end-group ($-SO_3^-$) and/or to decrease the pore size on the surface, Fig. 32.

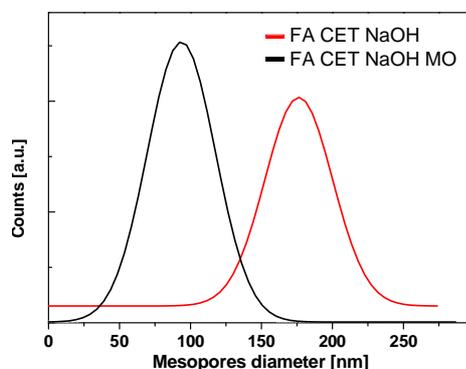


Fig. 32. The pores distribution on FA surface [239]

These chemical and structural changes are mirrored in morphology modifications, Fig. 33a and b, resulting in large differences in the substrates' affinity for heavy metals.

The various roughness values appear due to a complex of factors, involving alkaline oxides leaching, methyl orange treatment, and the formation new structures with important role in the heavy metals adsorption.

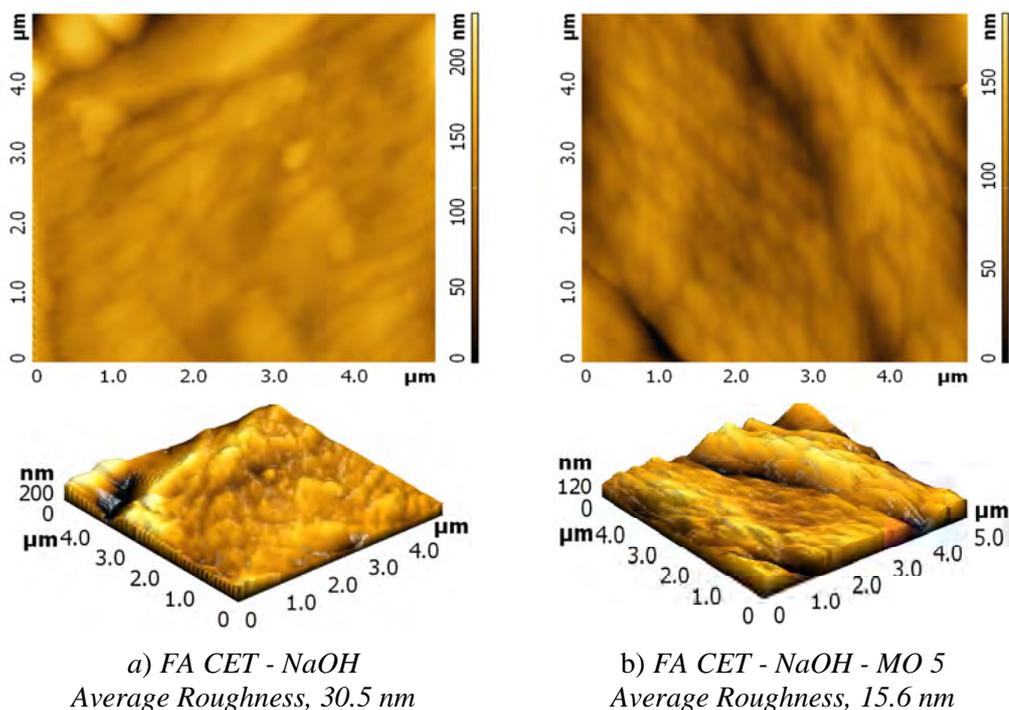


Fig. 33. AFM images [239]

Two heavy metal cations were selected to test the adsorption efficiency, based on their different polarizability. The Pb^{2+} and Zn^{2+} adsorption efficiency, η , on modify FA was evaluated to optimize the contact time and the amount of substrate for a given volume of pollutant solution. The residual metal concentration from the supernatant were analyzed by AAS, at $\lambda_{Zn} = 213.9$ nm and $\lambda_{Pb} = 283.3$ nm, after calibration.

The dynamic adsorption results are presented in Fig. 34 for the lead and zinc adsorption on FA-NaOH, compared with the results obtained using FA-NaOH-MO as adsorbents.

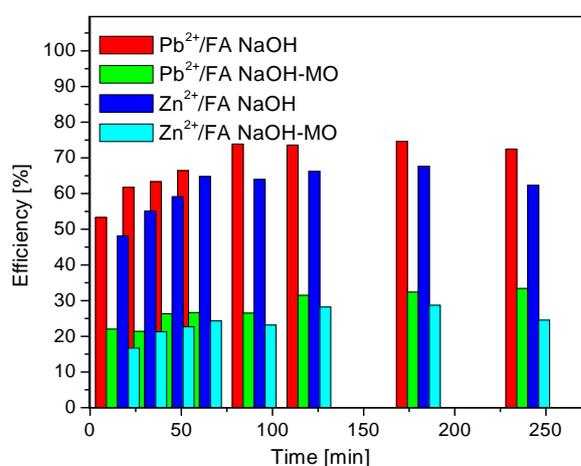


Fig. 34. Lead and zinc immobilization efficiency vs. contact time

The low adsorption efficiency of Pb^{2+} and Zn^{2+} cations on FA-NaOH-MO comparative with the efficiencies on FA-NaOH show that a share of pores are occupied with methyl orange molecules, as also supported by the AFM images and the average roughness values.

Increasing the amount of adsorbent from 0.5 g up to 3 g for 50 mL solution the initial pH increases up to 8 (still below the precipitation value) while the adsorption efficiency of the heavy metals increases as result of a larger amount of active centres in the system. The optimal adsorbent amount is found to be 1.5 g for Pb^{2+} cation removal respectively 1.25 g for Zn^{2+} .

So the optimal parameters to remove the metals ions (Pb^{2+} , Zn^{2+}) are:

- contact time: 60 min;
- m_{ss} in 100 mL solution, m_s : 1.25-1.5 g.

By comparing these results with those obtained in copper and cadmium removal for the same types of substrate the conclusion that can be formulated is upon the need for preliminary optimization studies for each type of pollutant/wastewater, prior the development of a scalable process.

The pseudo-second order kinetics did well apply to the majority adsorption processes.

The Pb^{2+} adsorption capacity on the investigated substrates was 94.3 mg Pb^{2+} /g FA-NaOH and 42.2 mg Pb^{2+} /g FA-MO-NaOH, respectively, showing a possible chemical adsorption, involving valence forces (through electrons sharing) between the adsorbent and the adsorbate.

The lead in aqueous solution may suffer solvation, hydrolysis or polymerization [240], forming many polynuclear species such as: $\text{Pb}_2(\text{OH})^{3+}$, $\text{Pb}_3(\text{OH})^{4+}$ which can be adsorbed. These larger compounds are more sensitive to the surface porosity, thus explaining the lower adsorption capacity of the MO-modified substrate.

The Raman spectrum show that in aqueous solution the zinc cations are hexahidrated $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$. The Zn^{2+} cation can interact with the MO molecules, forming stable complexes on the FA surface. Adsorption studies carried out to estimate heavy metal removal from wastewater, using fly ash, showed that the efficiency follows the order: $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ [241].

The adsorption isotherm data were experimentally obtained and the absorption parameters were calculated considering the Langmuir and Freundlich equations, respectively, as given below:

- The Langmuir model could better describe the lead and zinc adsorption on FA-NaOH-MO as result of a highly homogeneous substrate resulted after the dyes adsorption.
- The Freundlich model could better describe the adsorption of lead and zinc on FA-NaOH, the heterogeneous substrate.

III.5. Comparative Adsorption of Heavy Metals on Fly Ash and Wood Ash [242]

Fly ash, resulted from coal burning, and wood ash are mixtures mainly containing metal oxides and carbon in various proportion, depending on the initial raw material. Wood ash is expected to have a different composition and ionic degree, thus a significantly different surface charge.

As biomass use as energy raw material gains more and more attention, the use of wood ash as adsorbent for wastewater treatment might become an interesting recycling option. Therefore, comparative studies were done aiming at identifying similarities and differences between coaly fly ash and wood ash, and their potential use as adsorbents.

The raw materials were:

- (1) fly ash collected from the electro-filters of the CHP Brasov and
- (2) energetic willow ash (WA), resulted from burning a fast growing biomass, collected from the Thermal Wood Power Station Miercurea Ciuc.

The substrates were conditioned as optimized before, by washing and drying. Then the substrates were sieved and the 40-100 μm fractions were selected as substrate for experiments; they are noted FAw (Fly ash washed) and, respectively WAw (Willow ash washed).

The final pH and conductivity values of the supernatant were very different, proving that the raw ashes contain a quite different amount of soluble oxides (Na_2O , K_2O , lime etc.), exceedingly higher for the wood ash, Table 22.

Table 22. Conductivity and pH values in the washing water of the ash samples

Ash	pH	Conductivity [mS/cm]
FAw	6.6	1.46
WAw	12.2	17.96

The values confirm that the wood ash, particularly the willow ash has an increased content of potassium, magnesium and calcium oxides. Further XRD investigations were done to identify the differences between the FAw and WAw.

The XRD spectra, Fig. 35, show that the major components of both ashes are: carbon (graphite), SiO₂ (quartz) combined with Al₂O₃, hematite (Fe₂O₃) and MnO₂ (ramsdellite).

Phosphorous based compounds are also identified in WAw, as expected, considering the usual wood composition (with P amounting about 0.05% w). Although the main components are the same, the XRD data show that different crystalline structures can be expected, since the heights of the significant peaks largely vary between the two samples.

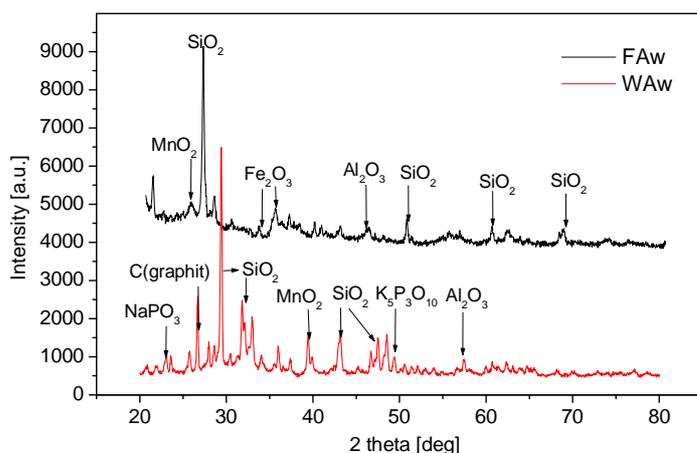
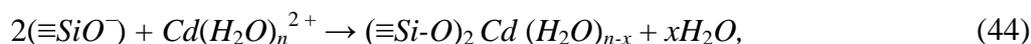


Fig. 35. XRD patterns of FAW and WAw [242]

Rich in silica and alumina, both substrates can form aluminosilicates with pH-dependent structures when hydrated. These groups can further dissociate, developing new active site ($\equiv\text{Si-O}^-$) ($\equiv\text{AlO}^-$), enhancing the negative surface charge which allows Cd²⁺ ions to form complexes at the surface (Eq. 44, 45) [243]:



The specific surface area of the ash samples was measured by BET-method and the results are presented in Table 23:

Table 23. BET area and porosity measurements for the ash substrates

Ash	BET-Area [m ² /g]	Micropores volume [cm ³ /g]	Micropores surface [m ² /g]	Average pores diameter [nm]
FAw	10.95	0.00081	4.07	25.6
WAw	14.74	0.00037	4.45	17.3

These values confirm a meso-porous structure of both types of ash and a rather high specific surface, with pores able to accommodate hydrated cadmium ions ($r = 0.426 \text{ nm}$) [244]. These values recommend as suitable the fraction chosen for experiments (aggregates with equivalent diameter lower than $100 \mu\text{m}$). It is also to notice that finer fractions (with equivalent diameter lower than $40 \mu\text{m}$) may raise technological problems in the adsorption steps. The AFM images in Fig. 36 show that the aggregates are developed by assemblies of grains, leaving wide open pores on the surface.

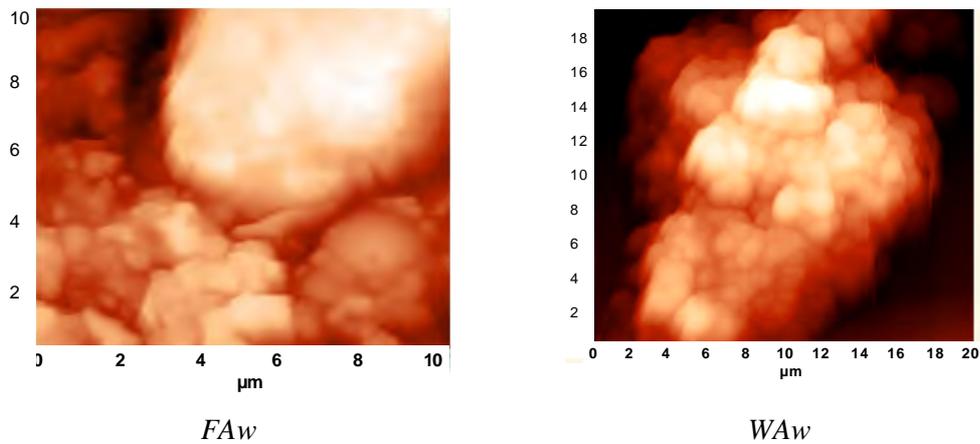


Fig. 36. The AFM topography of the samples [242]

The optimal contact time was evaluated using suspensions of 2 g ash in 100 mL solution. Aliquots were taken at certain moments (15, 30...360 min), when stirring was briefly interrupted and after decantation and filtration the volumes of supernatant were analyzed.

The effect of the contact time on the efficiency of the Cd^{2+} adsorption from single pollutant solutions is presented in Fig. 37.

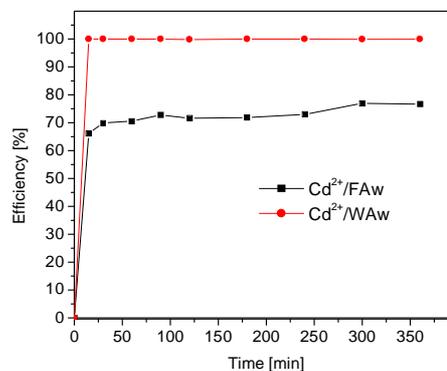


Fig. 37. Time influence on the Cd^{2+} ($c = 590 \text{ mg/L}$) adsorption efficiency from single pollutant solutions

The maximum of efficiency is obtained after 30 min, and was further used in experiments. Increasing the amount of wood ash substrate does not significantly alter the adsorption efficiency, as the data presented in Fig. 38 show. An amount of 2 g WA-W in 100 mL solution allows adsorption efficiencies over 90% both for single- and binary pollutant systems. On FAW, the optimal ratio is 3:100 g:mL.

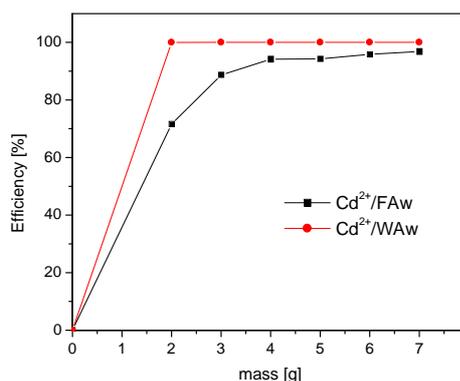


Fig. 38. Influence of the substrate mass on the Cd^{2+} removal efficiency

The Freundlich isotherm could describe the adsorption on both substrates, proving increased affinity for both species, on wood ash. The data also prove that the sites on the WA-W substrate are more active ($n < 1$, $n = 0.544$) in adsorbing cadmium and that there is a large cadmium adsorption capacity to be expected, in the optimized conditions.

The pseudo-second order kinetic applied to the investigated adsorption systems and shows quite slow process referring to cadmium: $k_2 = 0.201$ [g/mg · min]/FAw, $k_2 = 6 \cdot 10^{-5}$ [g/mg · min]/WAw, although there is a larger adsorption capacity: $q_e = 22.78$ [mg/g]/FAw respectively $q_e = 20.96$ [mg/g]/WAw.

III.6. Fly Ash Based Composite with Bentonite for Multi-Cation Wastewater Treatment [245]

Wastewaters resulted from many industrial processes, such as electroplating, inorganic pigment manufacturing, wood processing, petroleum refining etc. usually contain two, three or more heavy metal along with other pollutants. As their ionic radius and hydration number are different, eventually these cations will have different mobility and polarizability, thus different affinity in adsorption, for specific adsorption sites. Therefore, one alternative was to investigate a combination of substrates, based on fly ash and an abundant natural compound, bentonite or diatomite.

Bentonites are the most abundant argillaceous materials which can be used in wastewater treatment [245]. They are reported as low cost efficient adsorbents for some heavy metals (copper, lead, cadmium and zinc) while modified bentonite was used for removing ^{60}Co radionuclide from radioactive waste solutions. The outstanding adsorption capability is due to main mineral component as montmorillonite, smectite and clay.

There is a growing interest in using low cost adsorbents, fly ash, bentonite or their mixture. If these materials are characterized and tested to remove the heavy metals dyes, the adsorption process will be a promising technology.

Comparative adsorption studies were done using washed fly ash (FAw), bentonite (B) and their mixtures.

Bentonite was provided from NW Romania area. The raw fly ash was supplied by the CHP Plant Brasov, directly from the electro-filters, sifted, choosing a grains with diameter between 40-100 μm .

The major oxide components in fly ash and bentonite, with a certain influence in heavy metals and dyes removal are presented in Table 24. Using emission spectrometry other metals were also identified in small amounts (Ba, Cu, Sn, Pb, Cr, Ni, V, Zn, Ti).

According to the ASTM standards, the raw FA pertains of class F because the sum of the SiO_2 , Al_2O_3 and Fe_2O_3 is above 70% [226], while bentonite is of Na type [232].

Table 24. Adsorbent materials composition

FA Composition [%]									
Major oxides [%wt]									
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	LOI*
53.32	22.05	8.97	5.24	2.44	2.66	0.63	1.07	0.08	1.58
Bentonite Composition [%]									
Major oxides [%wt]									
72.11	14.92	2.62	2.31	2.12	1.34	1.91	0.62	0.05	2.06

Raw adsorbent materials contain soluble compounds, with pollution potential therefore washing before use is compulsory. By mixing 200 g of powder FA and separate 200 g of powder bentonite) with 2000 mL ultra pure water, followed by stirring at room temperature (20-22 °C), for 48 h till constant pH value. The pH and conductivity values were evaluated for FA (pH = 10.2 and for bentonite pH = 9.9, respectively $\kappa = 1.710$ mS for both). The washed FA and bentonite were further dried at 105-120 °C, till constant mass. These substrates are further denominated as FAw and B.

Structural and crystallographic properties of individual FAw and B particles were evaluated by XRD and for morphology studies by AFM images.

The images were taken in semi-contact mode with Golden silicon cantilever (NCSG10), with constant force 0.15 N/m, having the tip radius of 10 nm. Scanning was conducted on three or more different places with a certain area 10x10 μm or 5x5 μm for each position, chosen randomly at a scanning grate of 1 Hz. Further surface investigations were done using scanning electron microscopy (SEM) operated with SEM at an accelerating voltage of 20 KV. Compositions were measured using energy - dispersive x-ray spectroscopy (EDS). The BET surface and micro-porosity of the fly ash and bentonite was evaluated. The information related to the functional groups on the surface was provided by the FTIR data.

The diffractograms (Fig. 39) show that some crystalline phases of FA (quartz, philipsite cristobalite, hematite) are mostly present in raw FA and new crystalline phases appear (mullite) in FAw. The XRD data show that during washing soluble compounds concentrated on the fly ash surface are dissolved, leaving the core, with a different composition of non-soluble crystalline compounds, Fig. 39.

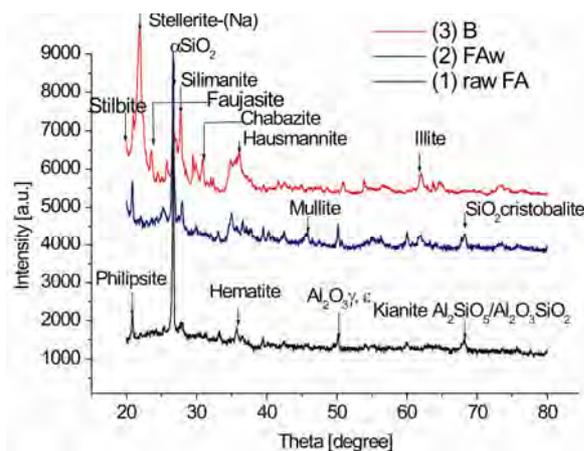


Fig. 39. XRD patterns of: raw FA (1); FAW (2); Bentonite (3) [245]

In bentonite the new crystalline phases are: sodium aluminium silicate NaAlSiO_4 , silimanite ($\text{Al}_2(\text{SiO}_4)\text{O}$), sodium aluminium silicate hydrate (phillipsite) ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12 \text{H}_2\text{O}$), silicate hydroxide hydrate (illite) ($(\text{KH}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$), chabazite-Na $\text{NaAlSi}_2\text{O}_6 \cdot 3 \text{H}_2\text{O}$, stellerite-Na, $\text{Na}_2\text{Al}_2\text{Si}_7\text{O}_{18} \cdot 7 \text{H}_2\text{O}$ faujasite silimanitul and other aluminosilicates phases, in lower amounts.

The main constituent of bentonites is montmorillonite, which is a 2:1 mineral with one octahedral sheet and two silica sheets, forming a layer. Layers are held together by van der Waals forces. Because of these weak forces and some charge deficiencies in the structure, water can easily penetrate these layers and cations balance the charge deficiencies [246]. The data also show that major components, quartz and graphite, are not affected during FA modification.

The crystalline degree of (B) is 79.5% the rest being represented by amorphous phases. The crystallites size, calculated with the Scherer formula ranges from 171.0 to 653.2 Å.

Supplementary information was obtained using the FTIR spectra. The FTIR spectra of FAW and Bentonite are presented in Fig. 40. The absorption band observed at $3622\text{--}3624 \text{ cm}^{-1}$ was attributed the hydroxyl group stretching/vibration in Si-OH, Al-OH-Al, Mg-OH-Al and/or Fe-OH-Al units in octahedral layer [29]. The asymmetric stretching mode of Si-O-Si in bentonite and FAW was suggested by the absorption band at 1010 cm^{-1} for bentonite and 1016 cm^{-1} for fly ash, both with sharp peak. In bentonite, water molecules are associated with the cations and are in some extent hydrogen bonded to the oxygen ions of the framework,

explaining the peak with less intensity, recorded at 1639 cm^{-1} which is characteristic of the bended mode in the water molecules. This observation indicates the similarity between bentonite and fly ash.

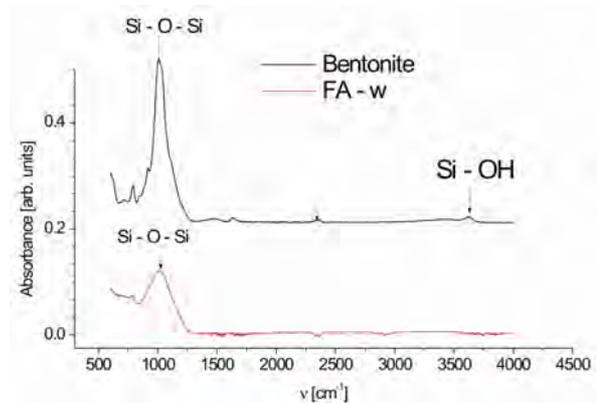


Fig. 40. IR spectra of Bentonite (-);FAw (-)

These data can be corroborated with the surface roughness which shows a strong decrease after washing of the fly ash Fig. 40. The roughness can give the different information versus the level of investigation (the millimeter scale usually permits one to distinguish the main surface treatments) [247].

Part of the oxides in raw FA and bentonite are water soluble. These chemical and structural changes are mirrored in morphology modifications, Fig. 41b and Fig. 41a and b resulting in large differences in the substrates' affinity for heavy metals. On phases distributions images there can be seen less agglomerates in new material adsorbent so more mesopores ready for to lodge the cations of heavy metals or dye molecules.

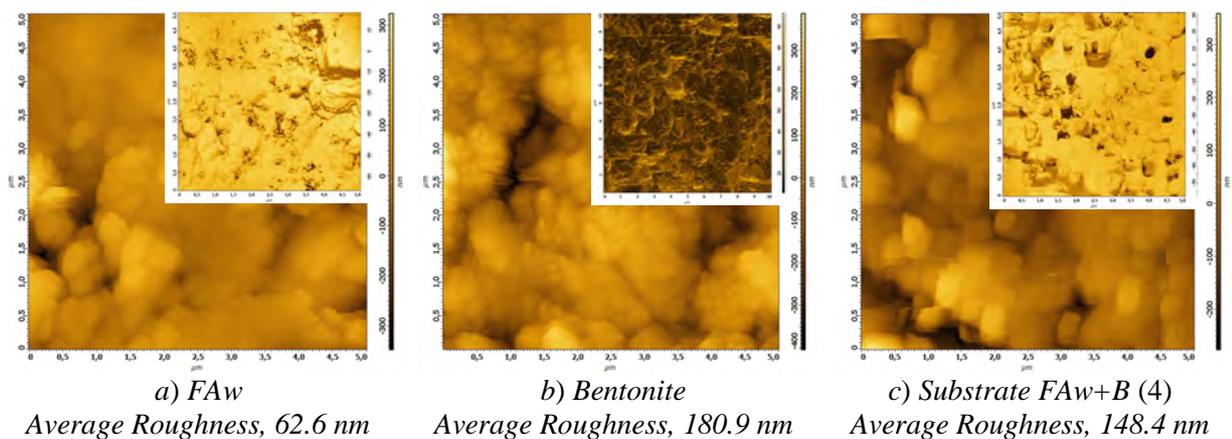


Fig. 41. The AFM topography and phase distribution [245]

These AFM images were used to characterize the surface morphology: the uniformity, grain size and pore size distribution of the samples Fig. 42.

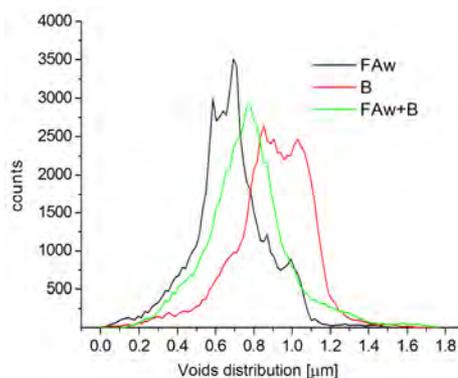


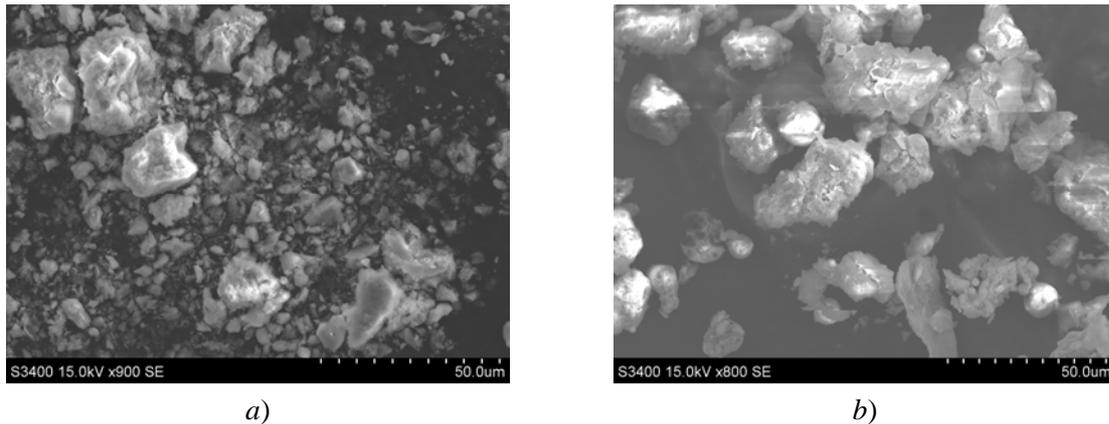
Fig. 42. *The interparticle voids distribution*

The surface area of the FAw and B were analysed and the results show a strong increase in the specific area surface, and a decrease in the average pores diameter; the mixed substrate (FAw+B) has average values showing that mechanical mixing is the most likely occurring process, Fig. 42.

Table 25. *Surface properties of FAw and bentonite*

Sample	Surface area BET [m ² /g]	Micropores vol. (t-plot) [cm ³ /g]	Micropores surface (t-plot) [m ² /g]	Average pores diameter [nm]
FAw	6.14	0.0004	2.25	27.2
B	21.33	0.0030	14.09	15.4

Adsorption and cation exchange capacities depend on the chemical nature of the sorbent surface, pore structure, size of the aggregates, crystallinity degree of the particles, thus the textural and structural features, but also on the cation present in the cell layer, the solution pH and temperature and the solution-adsorbent contact duration. In this view, bentonite adsorption strength due to fine particles is large, exhibiting a large contact surface. The surface characteristics for FA are presented in Table 26 and are characteristic to mezzoporous solids.



a) *b)*
Fig. 43. SEM images of Bentonite (a) and FAw (b)

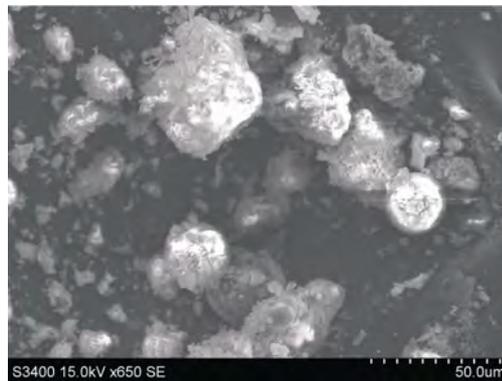


Fig. 44. SEM image of Faw+B loaded with Cd^{2+} , Cu^{2+} and MB

The SEM images (Fig. 43 and Fig. 44) show significant differences between the substrates: most FAw particles are spherical with diameters between 3.61 up 111 μm . The bentonite particles have a stratified structure with hexagonal large agglomerates, with sizes between 2.23 and 8.08 μm . The surface morphology of FAw and bentonite appears as corn flake crystals with fluffy appearance revealing the fine platy structure.

The results of the EDS analysis, Fig. 45 show that FAw and B have a similar composition that abounds in hydrous aluminosilicates. The EDS spectra of the materials Faw and B shown in Fig. 45 offered semi-quantitative ratio of present elements: O, Na, K, Ca, Mg, Al, Si, Ti, Fe. The analysis shows that the rims have a similar composition and abound the hydrous aluminosilicates.

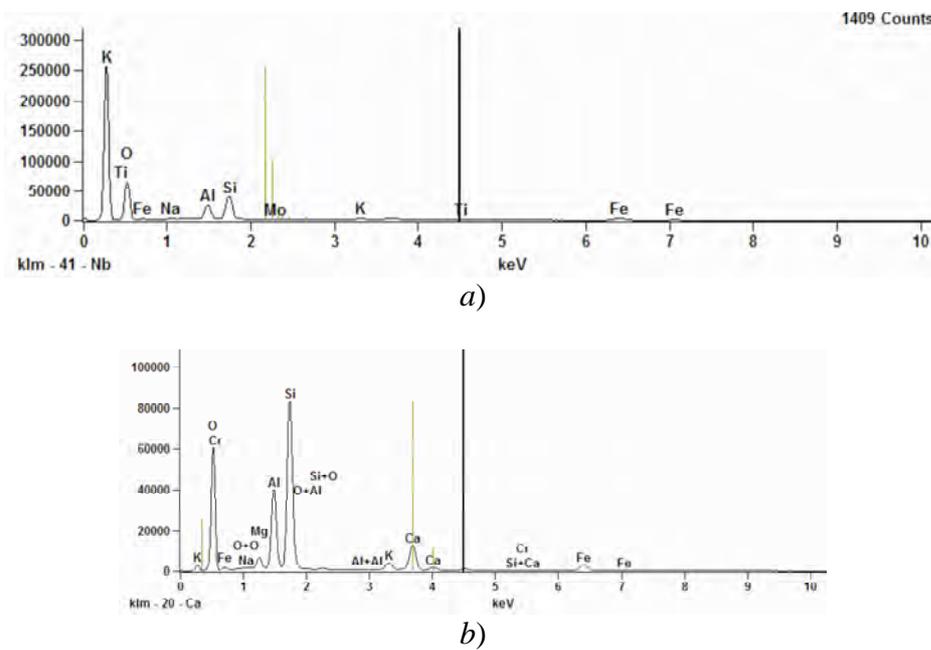


Fig. 45. EDS spectra of FAW (a) and Bentonite (b)

Bentonites are composed of largely hydrated sodium aluminosilicate (chabazite-Na $\text{NaAlSi}_2\text{O}_6 \cdot 3 \text{H}_2\text{O}$) which are capable of adsorption and ion exchange. Bentonites can form colloidal suspensions, gels and water molecules are adsorbed between the lattice planes in the movement of ions [248]. Cation adsorption involves mainly electrostatic forces therefore the surface energy of the new substrate (FAw:B) can strongly influence the adsorption process.

The polar and dispersive contributions to the surface energy of FAW, B and their mixtures were calculated according to the model developed by Owens, Wendt, Robel and Kaelble and are presented in Table 26.

Table 26. Surface energy data for the substrates

Substrate	Surface Energy [mN/m]	Dispersive contribution [mN/m]	Polar contribution [mN/m]
FAw	187.42	32.61	154.81
B	107.5	3.85	103.65
FAw:B (4)	330.79	89.62	241.17

The high global surface energy and a large polar component, recommending the material as a good adsorption substrate for heavy metals cations.

Adsorption tests were performed by batch experiments, under stirring up to 240 min at room temperature (20-22 °C), at the natural pH of the dispersion, Table 27.

Table 27. *The natural pH values of the suspensions with adsorbent*

FAw:B [g:g]	1:0	0:1	0.25:0.75	0.50:0.50	1.00:1.00	0.5:1.5
pH	7.4	9	6.2	5	5.1	6.5

Aliquots were taken each at 15, 30, 45, 60, 90, 120 180, 240 min., when stirring was briefly interrupted and the substrate was removed by vacuum filtration and the supernatant was analyzed by AAS. The absorbance measurements were recorded in the range of 200-900 nm, using a UV-VIS spectrophotometer at the maximum absorption wavelength registered at 664 nm.

Two series of experimental tests were done on mono solution with one pollutant Cd^{2+} ($c_{\text{Cd}} = 750 \text{ mg/L}$), using $\text{CdCl}_2 \cdot 2.5 \text{ H}_2\text{O}$, two heavy metals solution (Cd^{2+} and Cu^{2+} , $c_{\text{Cu}} = 400 \text{ mg/L}$), using $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$.

The lowest admissible discharge concentrations are, in most national regulations set for cadmium therefore, the optimized adsorption conditions set for cadmium were extended also for copper in multicomponent solutions, in the tests performed using FAw, B and their mixtures, as the Table 28 shows.

The optimal adsorbent mass: wastewater volume was evaluated based on cadmium 750 mg/L solutions, using a contact duration of 90 min, while the optimal contact time was evaluated on suspensions of 0.5 g FAw in 100 mL multicomponent solutions of Cd^{2+} and Cu^{2+} .

Table 28. *Substrates and pollutant systems experimentally tested*

Substrates (g) FAw: B	1:0	0:1	0.25:0.75	0.50:0.50	1.00:1.00
Substrate	(FAw)	(B)	(1)	(2)	(3)
Pollutant systems	Cd^{2+}	Cd^{2+}	$\text{Cd}^{2+} + \text{Cu}^{2+}$	$\text{Cd}^{2+} + \text{Cu}^{2+}$	$\text{Cd}^{2+} + \text{Cu}^{2+}$

The results proved that the pseudo-second order kinetic well describes the adsorption mechanism for both cations, on bentonite and theirs mixture the investigated substrates. The kinetic parameters are presented in Table 29 for cadmium.

Table 29. Kinetic parameters of the heavy metal removal on FAw:B mixed substrate

FAw:B [g:g]	Pseudo first-order kinetics		Pseudo-second order kinetics			Interparticle Diffusion		
	K_L [min ⁻¹]	R^2	k_2 [g/mg · min]	q_e [mg/g]	R^2	K_{id} [mg/gmin ^{1/2}]	C	R^2
Cadmium								
1:0	-	0.413	-	-	0.854	-	-	0.801
0.50:0.50	-	0.627	0.147	31.646	0.998	-	-	0.535
0.25:0.75	-	0.023	0.049	30.395	0.998	-	-	0.409
0:1	-	0.026	0.059	42.553	0.999	-	-	0.446
1:1	0.007	0.954	0.408	19.841	0.997	-	-	0.592
1.5:0.50	-	0.236	0.092	28.011	0.998	-	-	0.454

The adsorption efficiency, η , and adsorption capacity, q_m , were evaluated based on the optimal contact time, the mass balance and initial cations' concentration of adsorption for the most toxic heavy metal, cadmium. The efficiency was calculated using the following Eq. (46):

$$\eta = \frac{(c^i_{M^{n+}} - c^t_{M^{n+}}) \cdot 100}{c^i_{M^{n+}}}, \tag{46}$$

where ($c^i_{M^{n+}}$ and $c^t_{M^{n+}}$) are the initial and equilibrated cations' concentrations (mg/L).

The data allow optimising the adsorbent amount, considering cadmium as reference, in a single pollutant system.

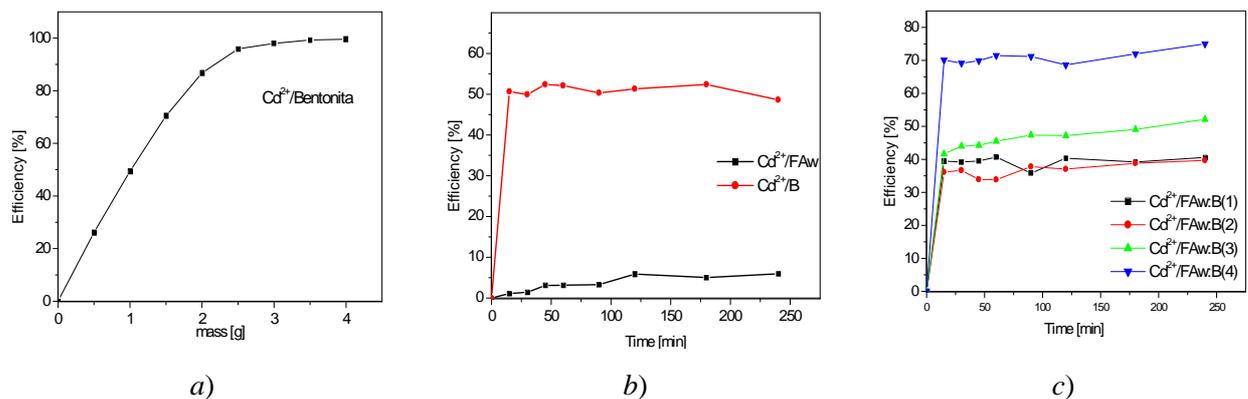


Fig. 46. Cd²⁺ immobilization: a) Efficiency vs. substrate dose, b) and c) Efficiency vs. contact time

Adsorption efficiency of cadmium on FAW is low because the surface of FAW is not activated and the specific surface area is low compared to bentonite.

The adsorption equilibrium for cadmium and copper needs 90 min to be settled therefore, this was the set as optimal time in all experiments. Also, for these two ions, higher substrate dosage is required, almost similar removal efficiencies (close to 70%) being registered at 2 g of FAW:B dispersed in 100 mL of solution. The removal efficiency increases with amount of bentonite from mixture, proving that adding B to FAW represents a path to fulfill the set target: the use of washed FA in advanced wastewater treatment.

The Cd^{2+} and Cu^{2+} cations can adsorb by chemically bonding with the active site ($\equiv\text{SiO}^-$) and ($\equiv\text{AlO}^-$) and can form complexes on the surface as presented by [248]. The metal compounds are the hydrated cations which can adsorb with partial or total de-hydration.

The Cd^{2+} and Cu^{2+} cations can also be adsorbend by the silanol group (Si-OH) of the layers, but theirs numbers is distinctly smaller (Eq. 47, 48):



where: $0 \leq x \leq n$ [249].

The FAW:B substrate is highly efficient (>90%) for the removal of all cations at concentrations below 100 mg/L, thus for advanced wastewater treatment, another preliminary process (e.g. precipitation) could be necessary.

The adsorption studies carried out to estimate the heavy metal removal from wastewater, using fly ash modified with bentonite, showed that the efficiency follows the order $\text{Cu}^{2+} \geq \text{Cd}^{2+}$, according with the dimensionless separation factors σ are: $\sigma_{\text{Cu}^{2+}} = 0.243 > \sigma_{\text{Cd}^{2+}} = 0.151$.

High adsorption efficiencies are registered for heavy metals concentrations below 100 ppm, recommending this substrate for simultaneous removal of heavy metals from wastewaters.

For cation mixtures similar results were obtained. Using as substrates FA, bentonite (B) and theirs mixture, the dynamic adsorption process of cadmium and cooper can be well describes with pseudo-second order kinetic equation. The kinetic parameters are presented in Table 30.

Table 30. Kinetic parameters of the heavy metal removal on FAw:B mixed substrate

FAw:B [g:g]	Pseudo first-order kinetics		Pseudo-second order kinetics			Interparticle Diffusion		
	K_L [min ⁻¹]	R ²	k_2 [g/mg · min]	q_e [mg/g]	R ²	K_{id} [mg/gmin ^{1/2}]	C	R ²
Cd²⁺ (Cd²⁺+Cu²⁺)								
0.50:0.50	-	0.415	1.613	24.752	0.948	1.505	0.851	0.942
1:1	0.022	0.843	0.379	10.341	0.998	-	-	0.547
1.5:0.5	0.013	0.967	7.330	20.877	0.982	-	-	0.867
Cu²⁺ (Cu²⁺+Cd²⁺)								
0.50:0.50	0.016	0.886	1.348	25.839	0.976	1.035	7.456	0.962
1:1	0.026	0.962	0.477	14.771	0.999	0.274	10.603	0.852
1.5:0.5	0.012	0.931	0.092	16.78	0.999	0.092	15.425	0.903

The data also prove that copper adsorption can follow more parallel mechanisms, which could be expected considering the FAw: B composition and/or the pores distribution with active sites of various energies. The values of the adsorption capacity on system FAw:B is found to decrease in the order Cu²⁺ > Cd²⁺ on mixtures 0.5:0.5 and 1:1. The amount of bentonite in mixture increase the adsorption capacity as expected considering the differences in the specific surface values between FAw and B because in aluminosilicates are more groups Si-OH that in FAw.

The dynamic adsorption results are presented in Fig. 47a, b for Cd²⁺ and Cu²⁺ from multi-pollutant systems.

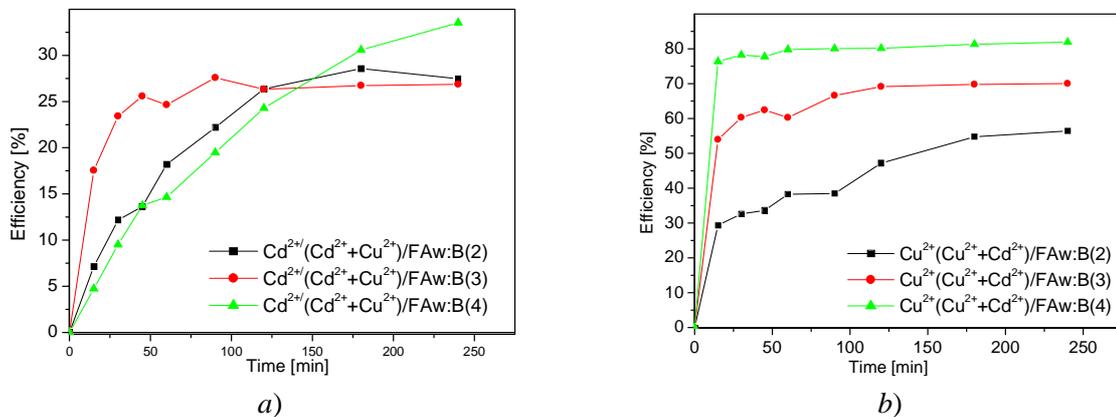


Fig. 47. Cd²⁺ and Cu²⁺ immobilization from multi-pollutant systems (a); efficiency vs. contact time (b)

Almost similar removal efficiencies (close to 70%) being registered at 2 g of FAW:B dispersed in 100 mL of solution. The removal efficiency increases with amount of bentonite in the mixture, proving its beneficial role in reaching the set target: the use of washed FA in advanced wastewater treatment. The FAW:B substrate is highly efficient (>90%) for the removal of all cations at concentrations below 100 ppm, thus for advanced wastewater treatment, another preliminary process like precipitation.

The adsorption studies carried out to estimate the heavy metal removal from wastewater, using fly ash modified with bentonite, showed that the efficiency follows the order $\text{Cu}^{2+} \geq \text{Cd}^{2+}$, and the dimensionless separation factors are: $\sigma_{\text{Cu}^{2+}} = 0.243 > \sigma_{\text{Cd}^{2+}} = 0.151$.

The data also show that cadmium and copper have a much lower affinity for the single bentonite substrate, showing an efficiency decrease for contact times longer than 240 min, supporting the assumption of an adsorption process without dehydration.

Further on, targeting up scaling, after adsorption and filtration the substrates loaded with pollutants were subject of pelletization, Fig. 48a then these were tested (a) at compression, Fig. 49b, Table 31.

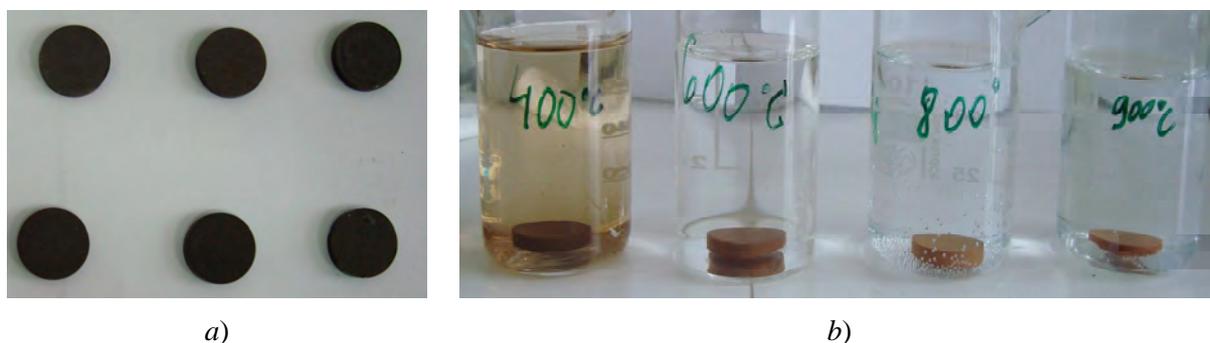


Fig. 48. The shape of pellets (a); stability tests in 100 mL water after 24 h (b)

Most stable are treatment thermic pellets at $900\text{ }^{\circ}\text{C} > 800\text{ }^{\circ}\text{C} > 600\text{ }^{\circ}\text{C}$.

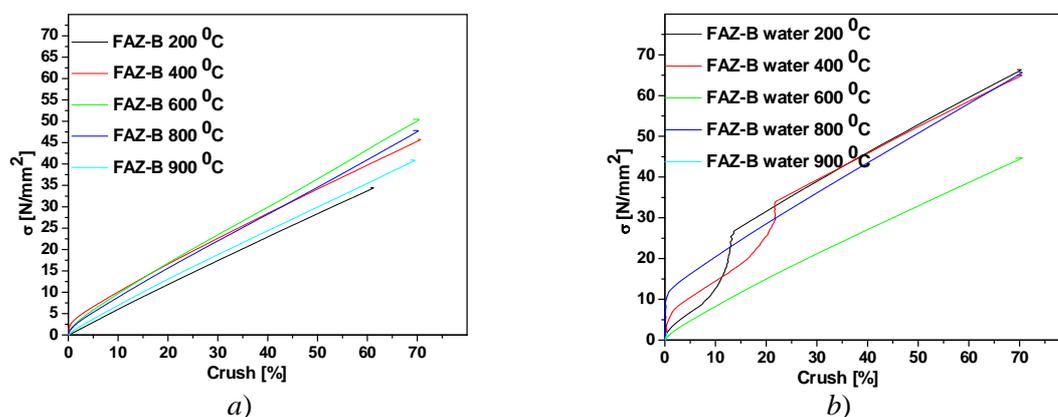
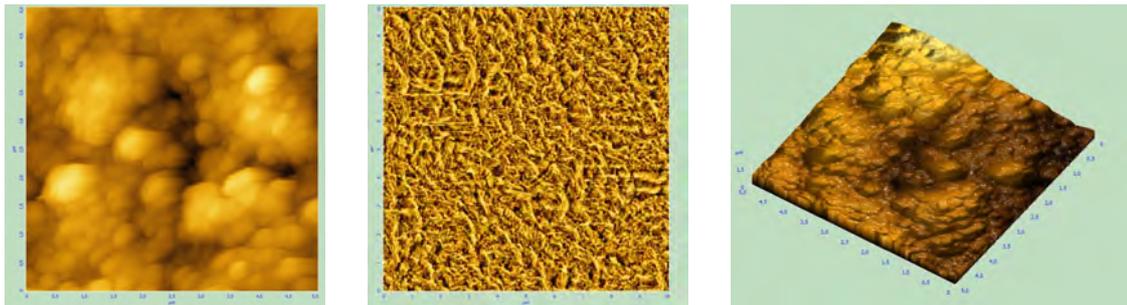
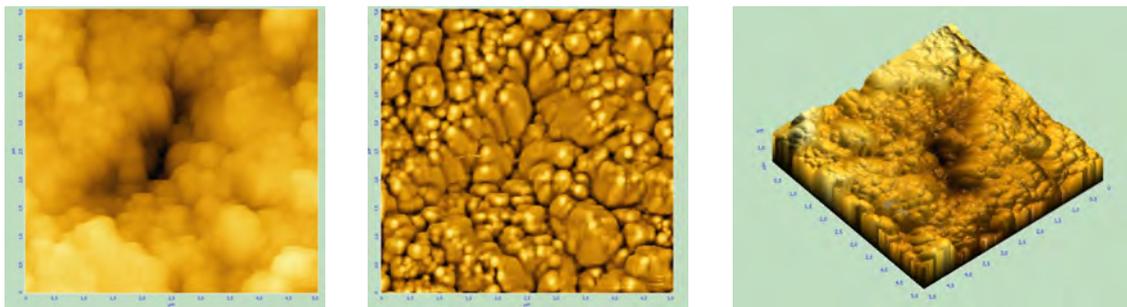
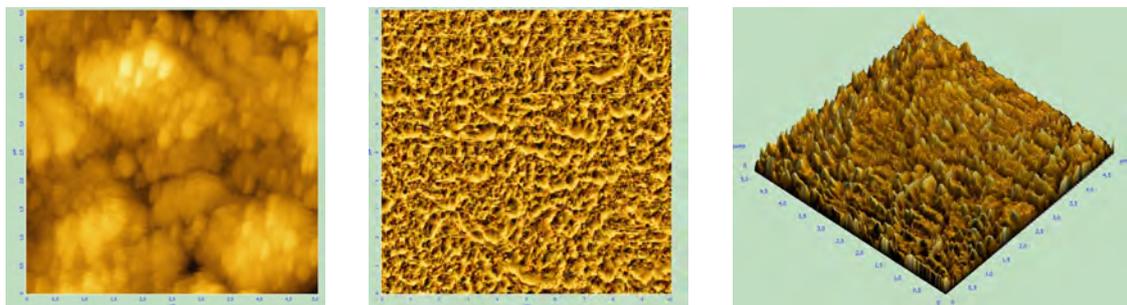


Fig. 49. Compression test: a) after thermal treatment; b) after 24 h immersion in water

Table 31. *The parameters in crush tests*

The sample	A [mm ²]	F _{max.} [N/mm ²]	ε F _{max.} [%]
FAZ-B 200 °C	314.2	61.23	34.42
FAZ-B 400 °C	314.2	70.64	45.71
FAZ-B 600 °C	314.2	70.38	50.71
FAZ-B 800 °C	314.2	70.21	47.78
FAZ-B 900 °C	314.2	69.54	40.89

**Fig. 50.** *AFM topography of powder - Phases distribution - roughness: 285.8 nm***Fig. 51.** *AFM topography of pellets - Phases distribution - roughness 242.7 nm***Fig. 52.** *AFM topography of pellets after thermic treatment (600 °C)
Phases distribution - roughness: 246.4 nm*

Round tablets (pellets) were annealed at different temperatures (200 °C, 400 °C, 600 °C, 800 °C and 900 °C). The five annealed samples, plus one which was not subject of heat treatment were introduced in 100 mL bidistilled water (each pellet in one glass). The stability of the

pellets strongly depends on the annealing temperature, and the best stability corresponds to the tablets annealed at 600 °C and 800 °C.

These pellets were tested as adsorbents in multicomponent solutions with the dye (MB) and heavy metals cations ($\text{Cd}^{2+} + \text{Cu}^{2+}$). The adsorption and photodegradation efficiencies were investigated using the most stable pellet (FA-B obtained at 800 °C) and TiO_2 , by six hours immersion and the results are presented in Fig. 53.

Methylene blue removal in adsorption (dark) and photocatalysis (under irradiation) was evaluated based on absorbance values, Table 32.

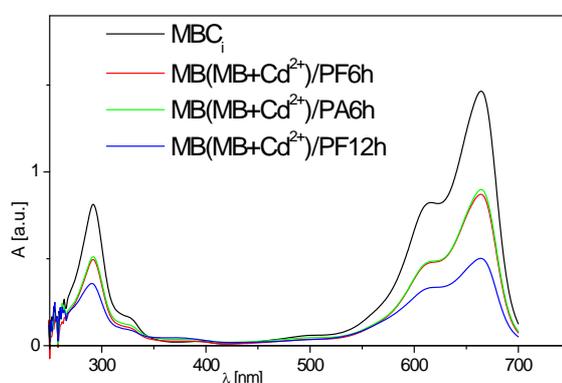


Fig. 53. The efficiency of MB adsorption from multicomponent solution on pellets

Table 32. Efficiency of adsorption MB from multicomponents solution (MB and HM)

$A_{\max, i}$ [nm]	$A_{\max, \text{Adsorption}}$ [nm]	$A_{\max, \text{Photodegradation - 6 h}}$ [nm]	$A_{\max, \text{Photodegradation - 12 h}}$ [nm]
1.464	0.8984	0.8716	0.5025
Efficiency [%]			
0	38.663	40.489	65.691

III.7. Fly Ash Based Composite with Diatomite for Multi-Cation Wastewater Treatment [249, 250]

In a similar approach another combination was investigated, based on a natural material (diatomite) and a waste (wood ash); this proved to be effective adsorbents for heavy metals. Preliminary long duration treatment by washing is required, as the substrates are firstly releasing soluble alkaline compounds. The washed substrates are noted Dw (diatomite) and WAw (wood ash).

The XRD spectra, Fig. 54a and b show crystalline structures both for Dw and WAw, the major components being carbon (graphite), SiO_2 (quartz) combined with Al_2O_3 , hematite (Fe_2O_3) and MnO_2 . Phosphorous based compounds are also identified in WAw, as expected, considering the usual wood composition (with phosphorus amounting about 0.05%-w). This similar composition supports the good compatibility of a future WAw-Dw composite.

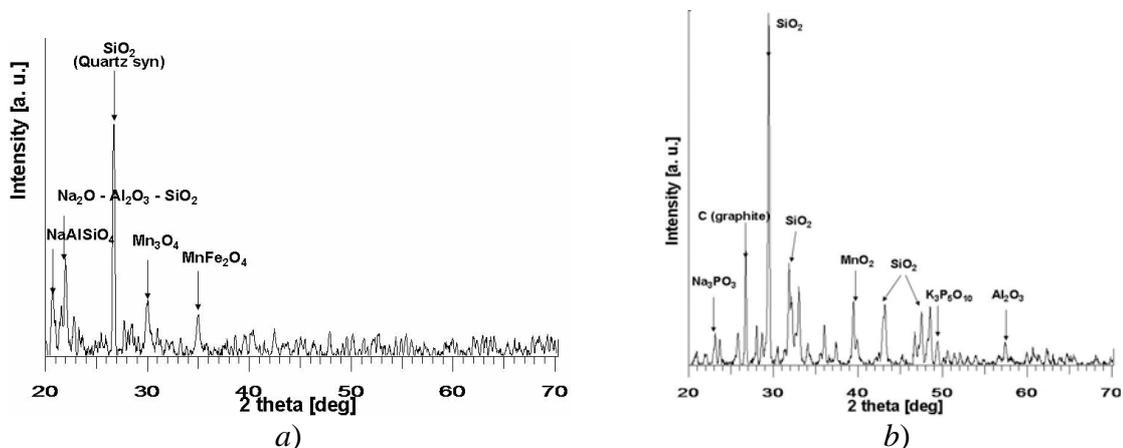


Fig. 54. XRD patterns of (a) Diatomite (Dw) and (b) wood ash (WAw) substrate [250]

The composition on crystalline phases of diatomite is: quartz syn (hexagonal) 52.17%, nepheline syn, NaAlSiO_4 (hexagonal) - 11.12%, sodium aluminium silicate, $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ - 23.91%, jacobite syn, MnFe_2O_4 (cubic) - 5.31%, manganese oxide, Mn_3O_4 (cubic) - 7.49%.

The predominant oxide composition, generally recognized as having negatively charged surface due to the oxygen surface ions, represents an asset in cations adsorption.

The solubilization/precipitation processes during washing lead to surfaces with broad open pores and an increased amount of active sites.

Further on, morphology is investigated as large specific surface is a second pre-requisite for a good substrate. As the images in Fig. 55 show, heterogeneous agglomerates are characterizing the materials and diatomite and wood ash grains are significantly larger (2.24...23.3 μm) than the individual particles.

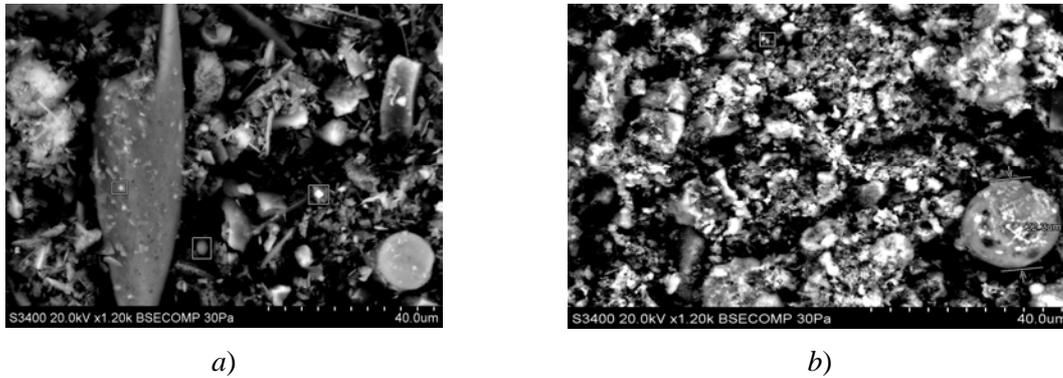
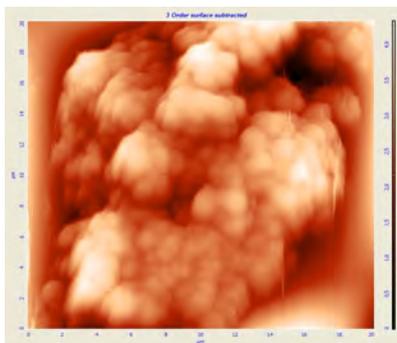


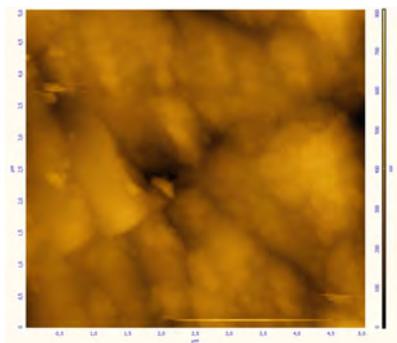
Fig. 55. SEM images of (a) Diatomite and (b) Wood ash grains

Fig. 56, that the aggregates are assembled in grains, leaving wide open and regular pores on the surface (in the micrometric range for fly ash and about ten times lower for diatomite).

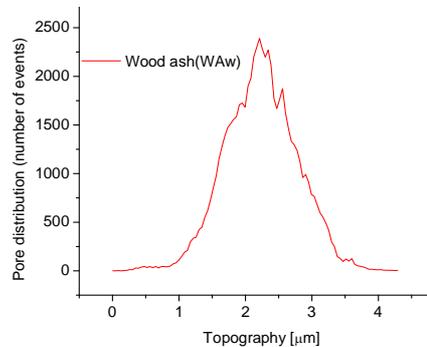
As both substrates are rich in silica and alumina, they can form aluminosilicates with different number of water molecules.



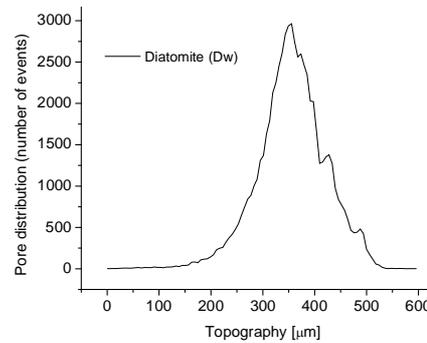
a) Wood ash; Roughness: 484.8 nm



b) Diatomite; Roughness: 210.7 nm



The interparticle voids distribution



The interparticle voids distribution

Fig. 56. AFM topography, average roughness and macro-pore size distribution in: a) wood fly ash; b) Diatomite

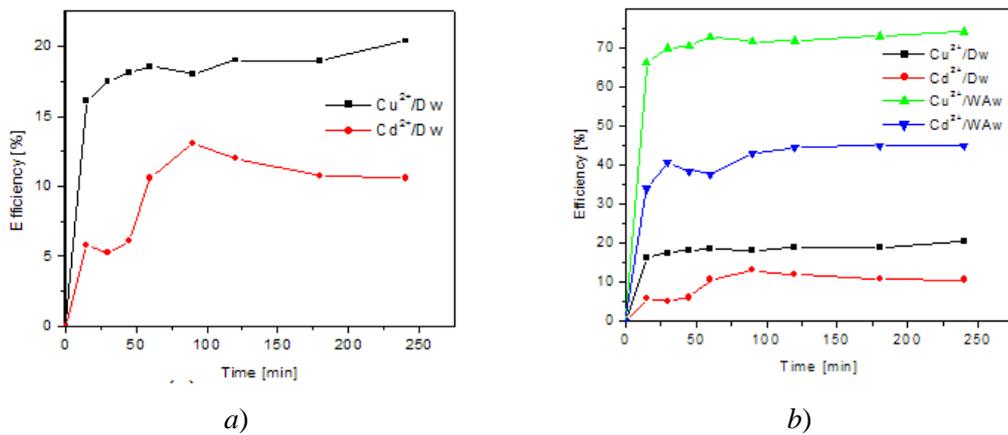


Fig. 57. Influence of the contact time on the adsorption efficiency of Cd²⁺ and Cu²⁺: a) on washed diatomite; b) comparative adsorption efficiency on washed diatomite

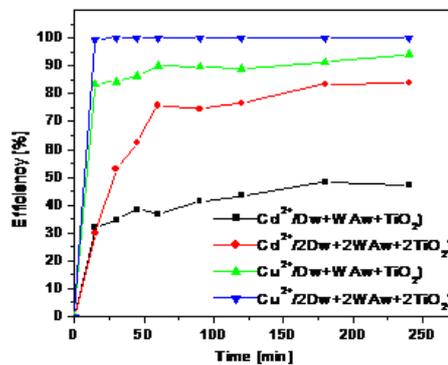


Fig. 58. Time influence on the Cd²⁺ and Cu²⁺ adsorption efficiency from three components system

The results show that the adsorption efficiency on diatomite is low and this can be a combined effect of the lower surface charge (as shown by the equilibrium pH) and lower specific surface. On the opposite, the results show the much higher affinity of both metal cations for wood ash, with higher negative surface charge (pH = 12.2) and larger specific surface.

To increase the specific surface and the oxide composition the WAw + Dw combination was mixed with the highly water-stable TiO₂ Degussa P25; previous investigations on coal fly ash (FAw) - TiO₂ mixtures outlined the optimal ratio FAw: TiO₂ = 3:1 [249]. In the current experiments the ratio Dw: WAw: TiO₂ was set at 1:1:1 (0.75 g). Two set of experiments were done for each cation, using an initial amount of composite substrate (Dw + WAw + TiO₂ = 0.75 g) and a doubled amount (2 Dw + 2 WAw + 2 TiO₂ = 1.5 g). The results obtained in optimized conditions showed an increase of the cadmium adsorption (up to 84%) and a strong increase of copper adsorption, up to 99%, Fig. 58. This proves once again the significant role of the small nano-

pores, corroborated with the actual size of the adsorbed specie, that influences the ionic strength and hydrated ionic radius (copper 0.295 nm < cadmium 0.426 nm).

The values of the kinetic parameters confirm the larger adsorption capacity of the novel mixed substrate (WAw + Dw + TiO₂), both for copper and cadmium. This values show the real potential of the concept hereby exploited, of mixing nano-sized, nanostructured powders with mezzo- or micro-sized grains of wastes or natural materials.

The results also show that this capacity is mainly linked to the very small pores, more difficult to access, thus leading to slower kinetics. The fastest process is observed - as expected for the adsorption of the small and mobile copper cation.

Table 33. Parameters of the pseudo-second order kinetics for copper and cadmium adsorption

Parameter	Cd ²⁺		Cu ²⁺		Cd ²⁺	Cu ²⁺
	Dw	WAw	Dw	WAw	Dw+WAw+TiO ₂	Dw+WAw+TiO ₂
q _e [mg/g]	9.329	20.964	9.268	13.2	49.51	54.95
k ₂ [g/mg · min]	1.157	6.10 ⁻⁵	0.721	0.247	0.382	0.401
R ²	0.979	1.000	0.997	0.996	0.997	0.981

The results, Table 33, confirm the larger adsorption capacity of the novel mixed substrate (WAw + Dw + TiO₂), both for copper and cadmium. This values show the real potential of the concept hereby exploited, of mixing nano-sized, nanostructured powders with mezzo- or micro-sized grains of wastes or natural materials. The results also show that this capacity is mainly linked to the very small pores.

III.8. Combined Fly Ash - Activated Carbon Composites for Heavy Metals Removal [251]

As the previous studies showed, mixed adsorbents have good potential for heavy metals removal and exhibit the advantage of tailoring the surface overall activity. Therefore, considering the well-known adsorption capacity of powder activated carbon (PAC), experiments were done to investigate the FA-PAC composites.

The powder activated carbon (PAC) has a good adsorption capacity for organic compounds (e.g. dyes), but has moderate efficiency for heavy metals. Due to its price, research is performed to replace PAC and one possible candidate is ash, mostly resulted from organic agricultural waste. Fly ash (FA) was tested and proved to be efficient in heavy metals removal. Simultaneous removal of heavy metals and dyes could be thus efficiently done using powder composites of PAC and FA.

Crystalline structure and morphology of the substrates were evaluated by XRD spectra of the substrates are presented in Fig. 59, showing that:

- (1) PAC has a low crystalline degree and carbon is the predominant component;
- (2) 24 hours of contact between FA and NaOH 2N solution is enough for removing the soluble compounds from the surface;
- (3) increasing the contact time to 48 hours does not bring any changes in the substrate composition;
- (4) the modified FA is rich in silica (quartz) and iron oxide (hematite) and contains a significant amount of carbon, explaining the affinity for substances with lower polarity.

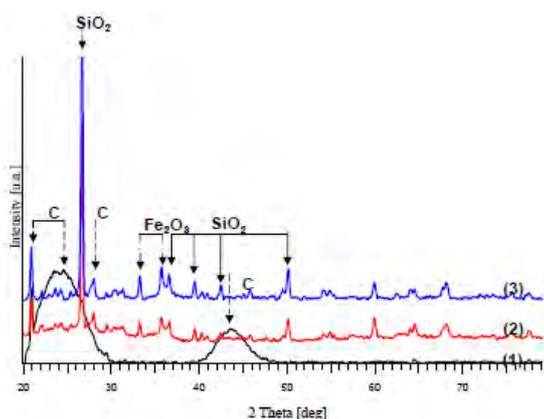


Fig. 59. XRD spectra:

- (1) PAC;
- (2) FA washed for 24 h in NaOH 2N;
- (3) FA washed for 48 h in NaOH 2N [37]

The AFM images (Fig. 60) show spherical aggregates, up to 100 nm, in PAC and irregular FA surfaces, with large grains.

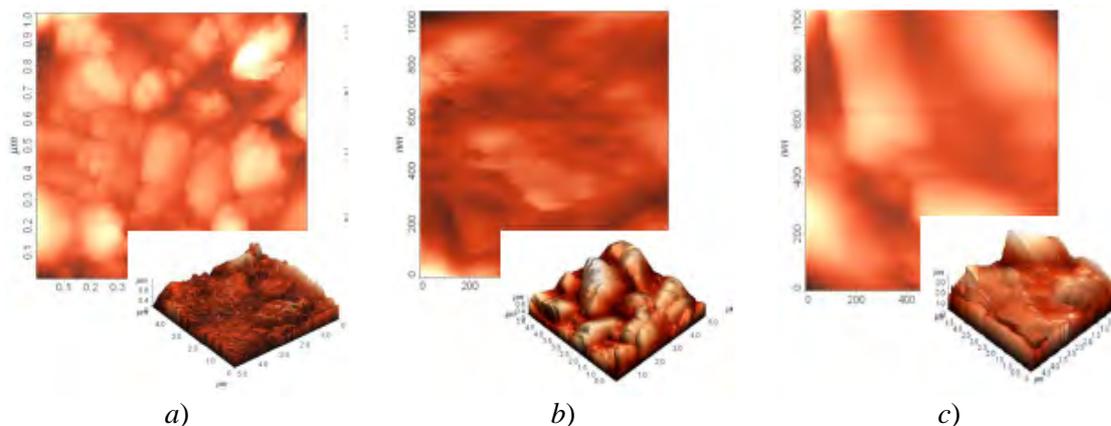


Fig. 60. AFM images of the samples: a) PAC; b) FA conditioned for 24 h in NaOH 2N; c) FA conditioned for 48 h in NaOH 2N [251]

The results proved that a 30 min contact time of the substrate with the pollutant(s) solution is enough to reach good removal efficiencies, and this was set as optimal value. Adsorption tests were done on substrates, varying the PAC amount, Fig. 61.

Experimental data show that the substrates containing only FA have a good affinity for cadmium (that can be explained due to the surface charge, as result of the rather large amount of carbon but this efficiency is increased when the adsorption occurs from mixed pollutant solutions of cadmium and methylene blue (MB), indicating a reciprocal conditioning effect of the inorganic/organic pollutants. This effect is most likely the result of a monolayer developed on PAC (as the MB adsorption as single pollutant runs with low efficiency).

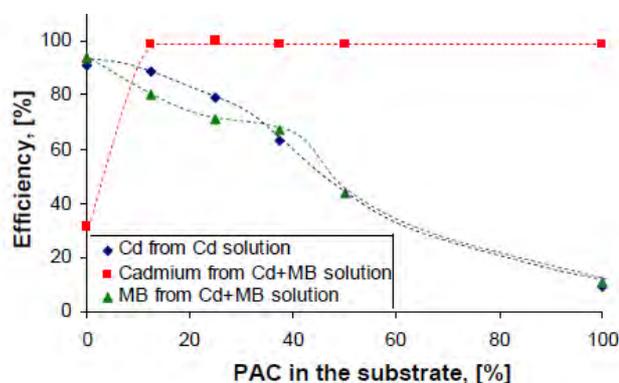


Fig. 61. Adsorption efficiency on mixed FA and PAC substrates

III.9. Fly Ash - TiO₂ Photocatalyst Mixed Substrates [224, 249]

Mixed substrates are efficient in adsorption, particularly in heavy metals adsorption. The second major step in the research line was to develop mixed substrates, active both in adsorption and photocatalysis. But, photocatalysis has an initial step adsorption; additionally, the heavy metals in the system can interact with the photocatalyst with consequences that should be controlled.

Therefore, preliminary adsorption studies (in dark) need to be done on these types of substrates.

III.9.1. Fly Ash CET/NaOH 2N - TiO₂

The start was done by a dynamic adsorption using two substrates: 1 g FA-CET/NaOH 2N (FA1) in 100 mL cadmium/cooper solutions and other 1 g TiO₂ (Degussa P25) in 100 mL cadmium/cooper solutions. The results are presented in Fig. 62.

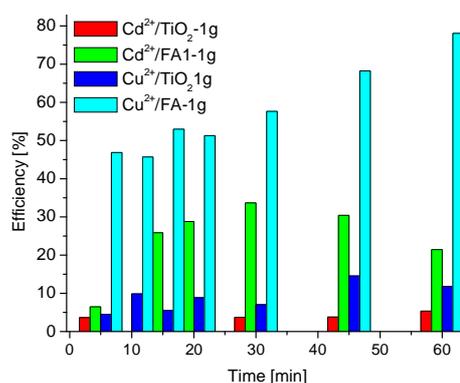


Fig. 62. Cadmium and cooper immobilization efficiency vs. contact time [224]

The influence of the TiO₂ over adsorption capacity was studied by modifying the ratio FA: TiO₂ (3:1; 2.5:1.5; 2:2; 1.5:2.5; 1:3) optimizing the contact time. The results presented in Fig. 63, show the best efficiency for cadmium and cooper obtained on two types of substrates: FA: TiO₂ (3:1; 2:2) at optimum ratio of 4:100 g/mL.

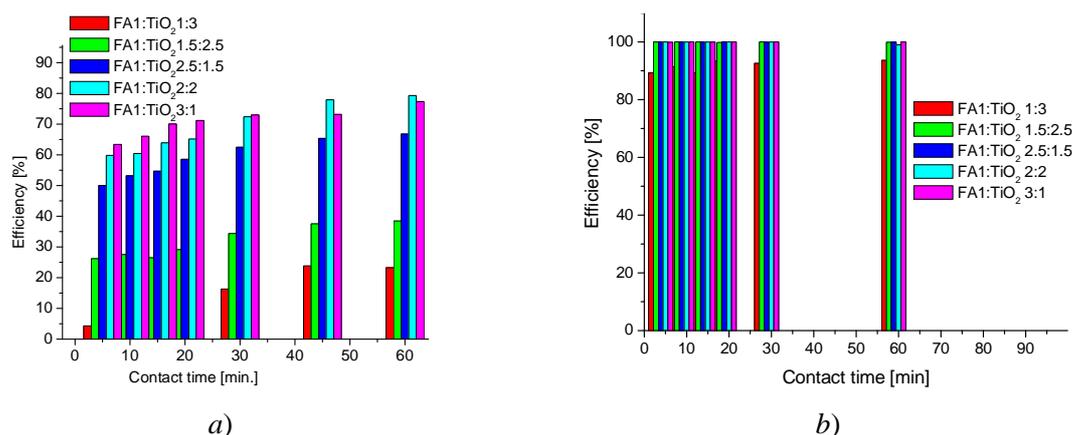


Fig. 63. Adsorption efficiency of (a) Cd²⁺ and (b) Cu²⁺ on mixed substrates (FA-CET-NaOH 2N : TiO₂) [249]

Mixed substrates, FA-CET/NaOH 2N, and TiO₂ (FA1-TiO₂) were used in dynamic adsorption tests, following the above optimized conditions: contact time of 30 min. and overall absorbent mass of 4 g in 100 mL cadmium/cooper solution.

For an initial cadmium concentration of 50 ppm, the required efficiency in a one step process able to fulfill the discharge regulations (<0.3 ppm) is 99.4%. High adsorption efficiencies, even at low cadmium concentrations when diffusion tends to hinder adsorption, are registered on substrates mixtures with the FA: TiO₂ ratios of 3:1 and 2:2 respectively, Fig. 63b.

Mixing TiO₂ with FA enhances the adsorption efficiency and rate, comparing with the single substrates thus, a synergic effect can be reported; a primary explanation is linked with the alkaline pH, induced by the modified FAs in the dispersion. The HO⁻ ions, negatively charge the amphoter TiO₂ (the zero charge point of TiO₂ is 6.2), activate the surface and increase the adsorption affinity for cations. This assumption is confirmed by the high adsorption rates in the 2:2 or 3:1 mixtures.

Adsorption of heavy metals on TiO₂ has a good efficiency but, in the experimental conditions, does not satisfy the wastewater discharge regulations for cadmium, especially at low initial concentrations.

Adsorption of heavy metals on modified fly ash has a good efficiency and mixture of modified FA and TiO₂ prove to be very efficient (with 1-3 orders in magnitude) in cadmium and cooper removal, strongly depending on TiO₂ content.

The pseudo-second order kinetics has the maximum rate constant for copper ($51.5 \text{ g/mg} \cdot \text{min}$) at a 2:2 ratio of FA:TiO₂. Two parallel kinetic mechanisms could be applied for majority adsorption processes: pseudo-second order kinetics and interparticle diffusion, confirming the high heterogeneity of the substrates.

The Langmuir model could not describe the cadmium and copper adsorption as result of a highly heterogeneous substrate, except the adsorption on mixture FA:TiO₂ = 1:3, with a surface more less heterogeneous because 3 g TiO₂ versus 1 g FA, proving that a mono-layer adsorption is possible. The Freundlich isotherm could better describe the adsorption and this is a supplementary prove that there heterogeneous substrates are developed by FA modifications. The experimental results show that this can be an up-scalable solution and represent a first stage in investigating the one step process of wastewater treatment in the textile finishing industry.

III.9.2. Fly Ash CET/Methyl Orange/NaOH 2N - TiO₂

As modified FA with MO proved a more predictable (although not more efficient) substrate, another set of experiments were done using FA-MO NaOH 2N substrate.

The study showed improved results obtained in cadmium and copper cations removal by using, the FA modified with methyl orange, with negative (HO⁻) surface charge and significantly improvement is registered when using mixed substrate (FA/MO/NaOH 2N+TiO₂). Adsorption efficiencies over 95% were registered on 25% TiO₂ mixtures with modified FA, both for cadmium and copper adsorption Fig. 64.

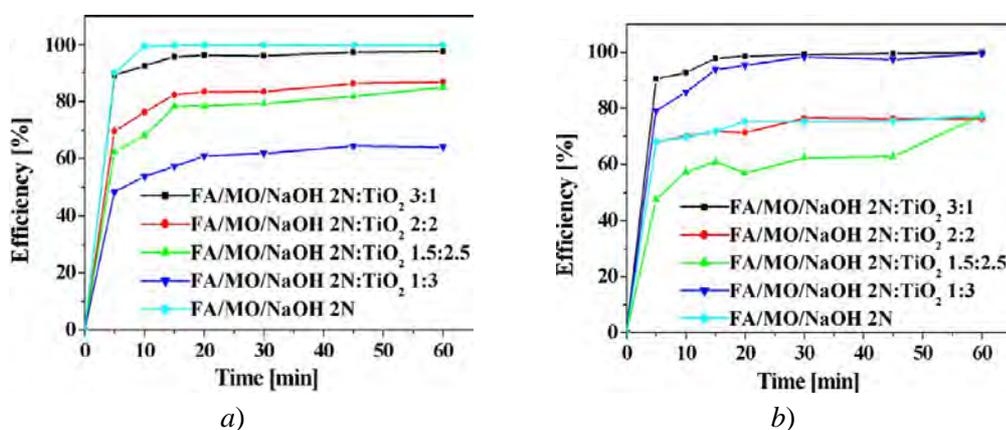


Fig. 64. Influence of amount of TiO₂ on the heavy metals removal: a) Cd²⁺; b) Cu²⁺ [224]

Various amounts of TiO_2 added to FA/MO/NaOH 2N can change the solution pH. Thus, at $\text{pH} > 6.17$ the surface charge is negative, favoring the cation adsorption. The data indicate a synergic effect regarding the adsorption of $\text{Cu}(\text{H}_2\text{O})_{6-x}^{2+}$ ions on the ash- TiO_2 substrates, especially at a 3:1 mass ratio of FA: TiO_2 .

Adsorption equilibrium of heavy metals ions (Cd^{2+} , Cu^{2+}) can be represented by the Langmuir and Freundlich adsorption isotherm. The results indicate that the Langmuir isotherm model can well describe the process on modified FA mixtures with TiO_2 , both for cadmium and copper. These results prove that the affinity of FA/MO/NaOH 2N and TiO_2 active sites is comparable and that chemical reactions are predominant. The substrates proved to have a larger affinity for cadmium, higher q_{max} values (>13 mg/g) as result of a higher ionic polarizability.

The kinetics of heavy metals adsorption can be modeled by various equations but the pseudo-second-order kinetic fits very well to all the processes data while the interparticle diffusion model described almost all the experiments. These show parallel kinetics, running on small and large pores.

A step forward was done by immobilizing the substrates, as these may represent a more feasible solution from the technological point of view.

III.9.3. Immobilization of the Adsorbents [252]

The adsorbent immobilization in thin films is beneficial since it requires less time, reduces the materials losses, the particle aggregation and skips the filtration steps.

Raw fly ash was used as a substrate for TiO_2 photocatalyst for purifying pollutants in air [253] but this cheaper titania-immobilized photocatalyst can not be used in wastewater treatment due to the soluble pollutants content.

This step of research [252] proposes an up-scalable option, combining the efficient adsorption process for heavy metal (cadmium and copper) removal and the dyes (MO and MB) photodegradation into a single step process.

The thin film substrates for heavy metal (cadmium and copper) adsorption and for photocatalytic studies (methyl orange and methylene blue photodegradation) were prepared by doctor blade (DB).

The paste was prepared by dispersing 0.5 g mixed of FA and TiO₂ powder (Degussa P25, 80% anatase and 20% rutile; specific surface area 50 m² g⁻¹ and a mean particle size of 30 nm) resulting in films with an average mass of 0.001 g. Four types of films were prepared in the following ratios FA:TiO₂ = 3:1, 2:2, 1.5:2.5, 1:3 and the results were compared with reference thin films of TiO₂. Thin films consisting only of FA presented poor adherence on the substrate under the testing conditions. The mixture was introduced into solutions containing ethanol, acetylacetone (C₅H₈O₂, 99.9%, Alfa Aesar) and triton X100 Sigma-Aldrich (non-ionic surfactant). The paste is smeared on a microscopy glass substrate (sample of 1.5x2.5 cm²) cleaned using ethanol, distilled water, acetone in successive sonication processes. After drying in air at 60 °C for about 10 min, the films were annealed in an oven at 500 °C, for six hours.

The films were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM).

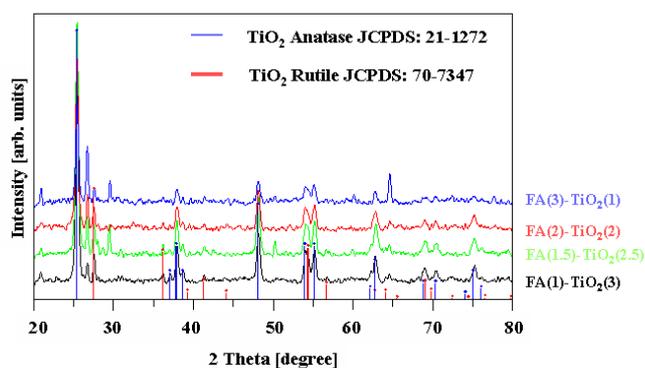


Fig. 65. XRD patterns for FA:TiO₂ catalyst [252]

The XRD spectra show that the major components of the mixed substrate are, beside TiO₂ anatase (JCPDS: 21-1272) and rutile (JCPDS: 70-7347) those resulted from FA: carbon, SiO₂ in various structures (cubic, rhombohedral) combined with Al₂O₃ as silimanite (Al₂SiO₅), mullite (3 Al₂O₃ · 2 SiO₅), along with γ -Al₂O₃, hematite (Fe₂O₃) and CaO.

The AFM image display high quality and porous mezo-crystalline structures Fig. 66.

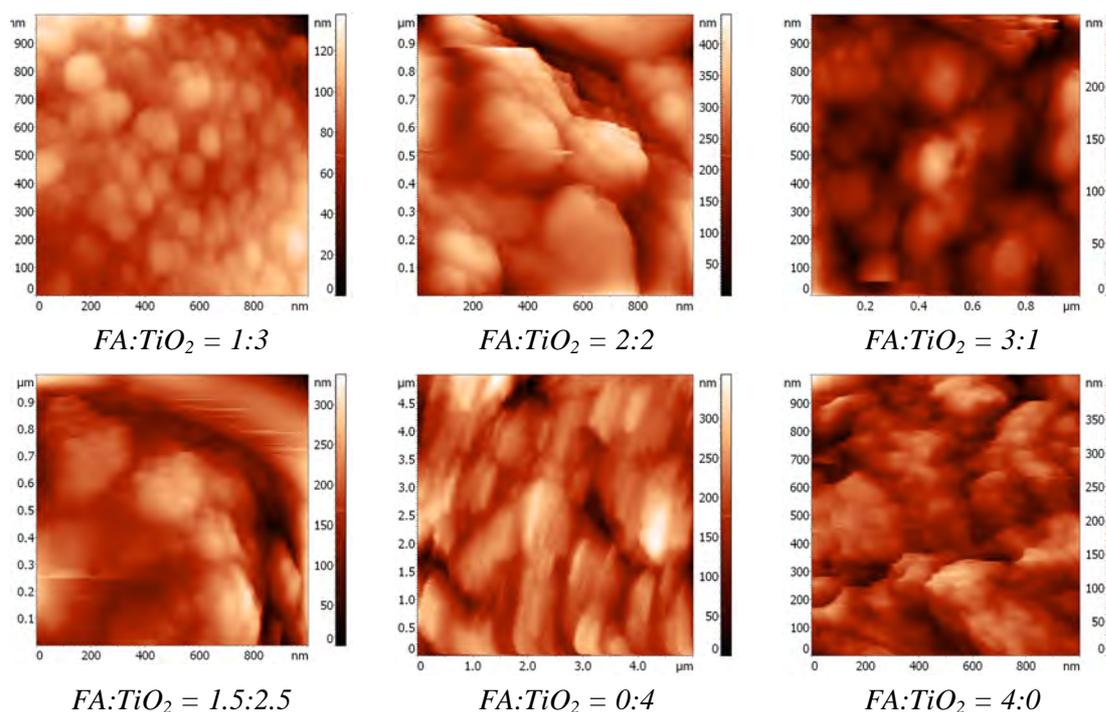


Fig. 66. The AFM topography of FA:TiO₂ film [252]

The films present a granular structure consisting of interconnected grain particles resulted from crystallite aggregation. The higher roughness of the TiO₂-DB film allows a good ability to capture the incident photon energy since a large surface favours the photodegradation process and well accommodates adsorption.

The image analysis of the surface topography can provide detailed information on the surface pore structure and allows quantitative determination of the pore size distribution, Fig. 67. The pore size analysis shows that micro-, meso- and macroporosity are far from being clearly and sharply defined. The highly heterogeneous surface aspect correspond to the films with equal (2:2) and close to equal (1.5:3.5) FA:TiO₂ composition.

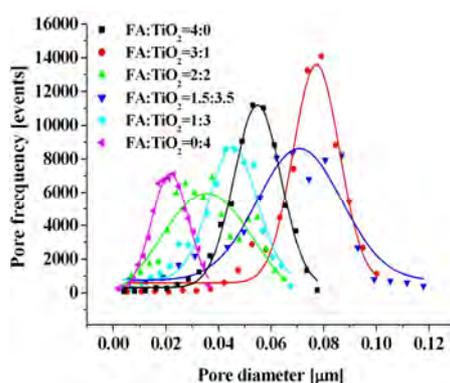


Fig. 67. The pore size distribution of FA:TiO₂ composites

The optimized results presented on thin films consisting of mixed FA and TiO₂ were obtained at much longer contact time, of 360 min (the optimised duration for photodegradation), considering the final use of these films in a single step process for simultaneous removal of dyes and heavy metals.

Considering the efficiency/adsorbent mass ratio, the adsorption process can be considered efficient. The highest adsorption efficiencies at low concentrations (advanced wastewater treatment), for both cations were registered for the samples with the largest pore distribution.

The substrates are highly heterogeneous in terms of composition thus, not surprisingly; the process could not be modeled using the Langmuir equation (although chemo-sorption is the most likely process). Still the Freundlich Equation could be used to fit the experimental data for most of the tests. The results of the adsorption test on thin films, the Freundlich parameters, are presented in Table 34:

Table 34. Cadmium and copper adsorption on thin films of FA and TiO₂

FA:TiO ₂	Freundlich parameters			Efficiency [%]	
	k	n	R ²	C _i = 30 ppm	C _i = 485 ppm
Cd²⁺					
3:1	1.148	0.815	0.970	13.4	12.0
2:2	0.867	0.860	0.795	15.0	5.9
1.5:2.5	1.139	0.810	0.911	24.3	14.0
1:3	1.265	0.890	0.920	18.1	8.85
Cu²⁺					
3:1	10 ⁻⁶	0.297	0.824	6.9	9.8
2:2	0.898	0.865	0.823	13.9	9.3
1.5:2.5	0.882	0.867	0.919	12.6	10.3
1:3	1.63	1.057	0.885	11.5	5.5

The result indicate that the FA:TiO₂ mixed can be used for MO and MB photodegradation. An activation effect of TiO₂ was observed for FA:TiO₂ = 2:2 weight ratio. The methylene blue photodegradation efficiency was 40% for UV/O₂ system and the efficiency increased up to 85% for UV/H₂O₂ system due to the alkaline pH induced by the fly ash. The films presented good cadmium and copper adsorption efficiency but an increase of the substrate amount is required.

III.10. Fly Ash - WO_3 Photocatalyst Mixed Substrates [254]

The traditional adsorbents such as activated carbon, zeolites and oxides (TiO_2 , WO_3 , SnO_2) have high metal adsorption capacities, but are generally expensive.

Literature mentions that WO_3 is a wide band gap semiconductor (2.8 eV) with optoelectronic properties, and experimental studies proved that it can be also used as photocatalyst, replacing anatase TiO_2 which has a higher cost. The couple semiconductors systems (WO_3/TiO_2) have been investigated [255] and for these WO_3 proved to lead to systems that can be activated by visible light irradiation.

The fly ash contains various oxides among: TiO_2 , Fe_2O_3 , MnO accelerating (handing) the photocatalytic activity of WO_3 . Other hand the efficiency of fly ash in the treatment of wastewaters loaded with dyes and heavy metals can be improved by adding WO_3 [254], thus combining adsorption and photocatalysis based on a mixture of catalysts and fly ash.

Previous results were presented when using TiO_2 as photocatalyst/adsorbent.

Other research presents the results when using a mixture of WO_3 and FA CET Brasov, in a one step treatment process of wastewaters containing the cadmium ion. The process efficiency and kinetic is reported and correlated with the substrates characteristics.

Single substrates (FA and WO_3 respectively) were used in adsorption tests as dispersions (2 and 3 g) in 100 mL cadmium solutions 0.01N. High efficiencies, up 99%, are obtained when 3 g FA/NaOH 2N was used for adsorption, and up 82% for the 2 g FA/NaOH 2N substrate.

Despite the efficiency, higher solid phase concentration has the drawback of increased turbidity that can reduce the further photocatalytic efficiency, due to lowering the light amount. Therefore, further adsorption studies will be done on 2 g modified fly ash.

AFM data, Fig. 68. were used to get supplementary information about the FA macro-pores resulted from particles associations. Large pores are developed as result of particle aggregation. As the images in Fig. 69 SEM. Shows, the FAw grames are significantly large (27.6 micro m - 111 micro m that the FA- WO_3).

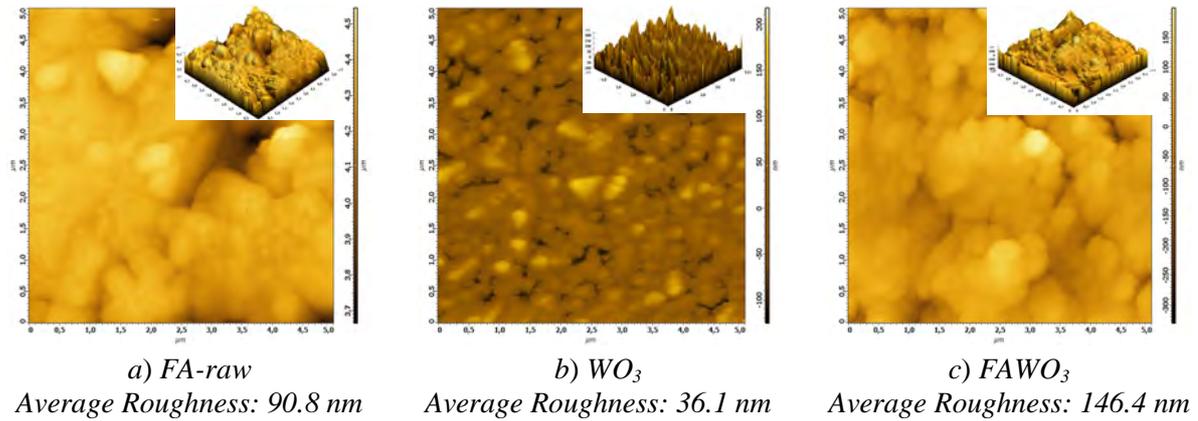


Fig. 68. AFM topography and average roughness

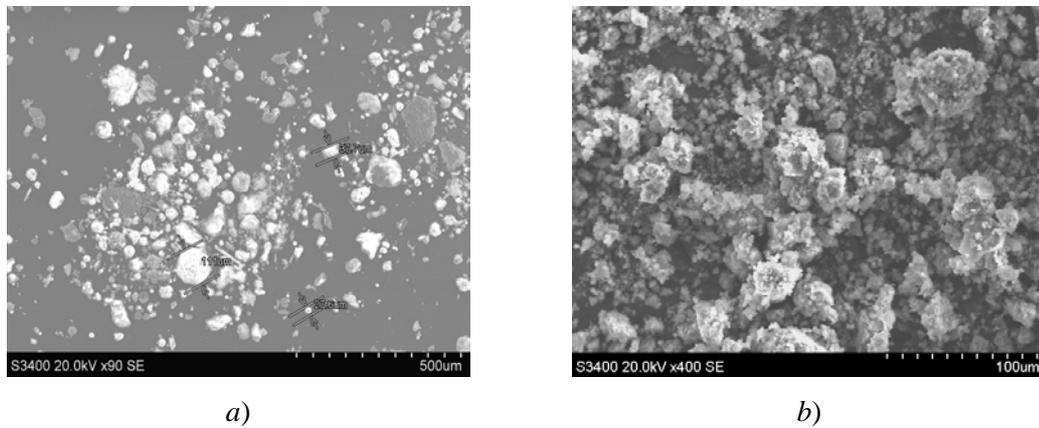


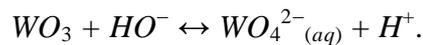
Fig. 69. SEM images of FAw (a); FA-WO₃ substrate (b)

The interactions between the ash and sodium hydroxide develop new active sites ($\equiv\text{SiO}^-$) and ($\equiv\text{AlO}^-$), allowing metals to form complexes on the surface (Eq. 49, 50) [243]:



On the amphoteric WO_3 , the protolytic equilibrium can lead to various surface charges, according to the solution pH and the point of zero charge of the WO_3 ($\text{pH}_{\text{pzc, WO}_3} = 4.2$), [256]:

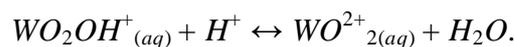
- In strong alkali solution WO_3 can interactions with HO^- will be possible the reaction:



Close to the point of zero charge $\text{pH} < \text{PZC}_{\text{WO}_3}$ is possible the dissolution of the solid WO_3 :



- In strong acidic solution the process can continue:



Consequently, at the solution pH (5.8), WO_3 is predominant negatively charged (WO_4^{2-} (aq)), enhancing the heavy metals adsorption.

The negative efficiency for Cd^{2+} removal on WO_3 at pH 5.8 can be explained not as desorption but as an apparent increase in the cadmium concentration due to water binding; the tungsten oxide, WO_3 can form new species of metawolframats $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ [255] or can largely host water chemisorptions forming new $\text{W}=\text{O}$ binds.

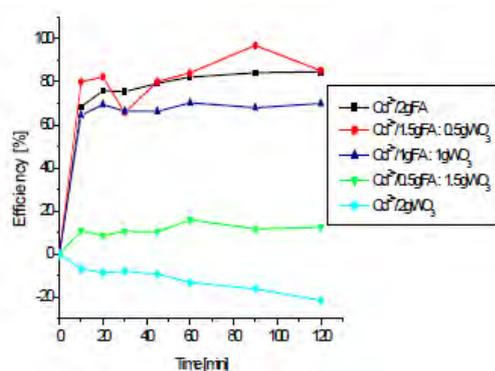


Fig. 70. Cd^{2+} immobilization efficiency vs. contact time

If there is a large amount of immobilized water molecules, the amount of free solvent species is strongly decreased and the cadmium equilibrium concentration is apparent higher than the initial one, in a process similar to the “salting out” effect.

On the other hand, the water absorbed is a new sources of protons $[\text{H}_3\text{O}^+]$ which disadvantageous the adsorption of heavy metals. Amounts of WO_3 catalysts added at FA can improve the cadmium adsorption capacity of the substrate and solve both problems: the dyes photodegradation and the heavy metals removal. The best Cd^{2+} adsorption efficiency occurs on mixtures containing 75% FA and 25% WO_3 at the pH 8.3 (Fig. 71).

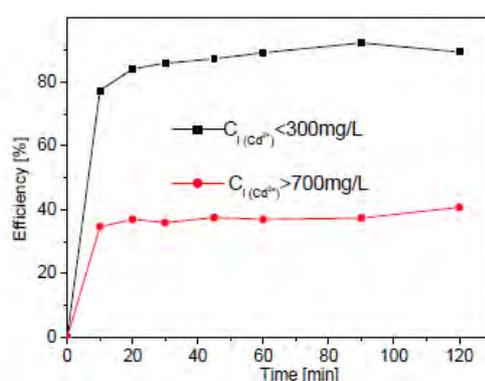


Fig. 71. Cd^{2+} immobilization efficiency from (Cd^{2+} + MB) vs. contact time on the 75% FA:25% WO_3 substrate

The FA has an open pores morphology and the adsorption efficiency of MB is good, Fig. 72, while the cadmium adsorption depends on the FA fraction used, being negative on substrates of pure WO_3 , when the salting out effect can be supposed. The pseudo-second order kinetics describes well all the processes, at average and low cadmium initial.

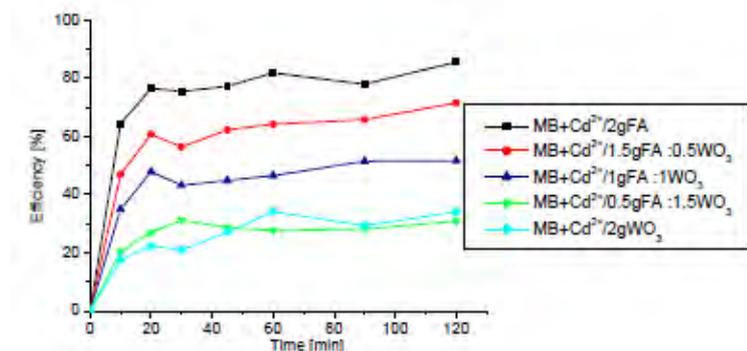


Fig. 72. MB immobilization efficiency vs. contact time on various substrates of FA with WO_3 from $(Cd^{2+} + MB)$ aqueous solutions

III.11. Fly Ash Based Adsorbents for Dyes Removal [257, 167, 259]

The aim of the entire research program is to identify novel and versatile solutions, based on fly-ash for advanced wastewater treatment with complex pollutant load.

So far, there were presented various alternatives for heavy metals removal from single- and multiple-cation solutions.

The next step was to test the most promising substrates for dyes removal. Dyes were chosen for several reasons:

- textile and dye-s production industries are responsible for huge amounts of wastewaters, worldwide;
- dyes are difficult to (bio)degrade and to mineralize as being quite stable compounds (a pre-requisite for their use);
- traditional processes (adsorption based) usually are not able to completely remove dyes. Alternative membrane processes are efficient but expensive.

Thus an alternative is their removal by photocatalytic processes.

As outlined, most of the dyes are discharged along with other pollutants like heavy metals and surfactants. Thus combined adsorption and photocatalysis processes are required. The aim of the research was to combine these processes in a single technological step.

As the complexity of the pollutants systems increase, concurrent processes are expected. To understand these, reference studies should be developed for each possible mechanism. This is why, adsorption tests of dyes were done on the most promising substrates, previously described.

As reference dyes there were used methyl-orange and methylene blue as these are recognized as chemically stable and as they have quite different molecular structure.

Methyl-orange was used as standard in many studies because it has a remarkable stability to photo-degradation.

The substrate: modified fly ash collected from S.E. Hunedoara Deva (Mintia) (FA-M), and its mixtures with TiO_2 (FA-M + TiO_2) were used in pollutant system with a mono-component of MO by $C_1 = 10^{-4} \text{ mol L}^{-1}$; $C_2 = 5 \times 10^{-5} \text{ mol L}^{-1}$, and chosen as they represent a usual upper limit of the industrial wastewaters subject of investigations.

The XRD data, Fig. 73, also show that FA contains small amounts of crystalline titanium oxide (as brookite and as non-stoichiometric Ti_4O_7) thus indicating a possible photocatalytic activity. Other crystalline oxides are also part of fly ash, as bixbyite (Mn_2O_3) commonly found with hematite that can be responsible for in situ oxidation/reduction systems of Fenton type. The unburned carbon, as micro-sized crystallites is part of the FA and can explain the versatility of this material in various adsorption processes. All these components are characterizing the raw fly ash and can be found also in the modified FA.

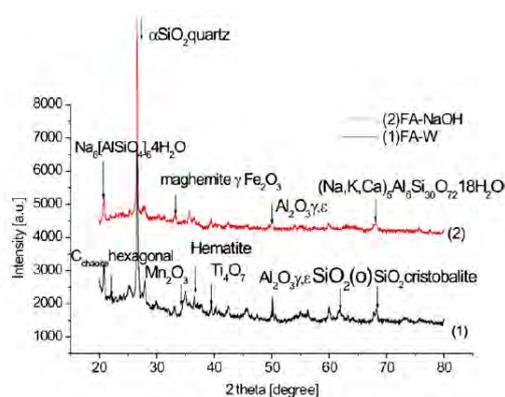


Fig. 73. XRD of raw FA, washed (1), and conditioned with FA-NaOH (2)

Based on the method proposed by Otero et al. [258], the AFM data, Fig. 74, were used to get supplementary information about the FA macro-pores resulted from particles associations.

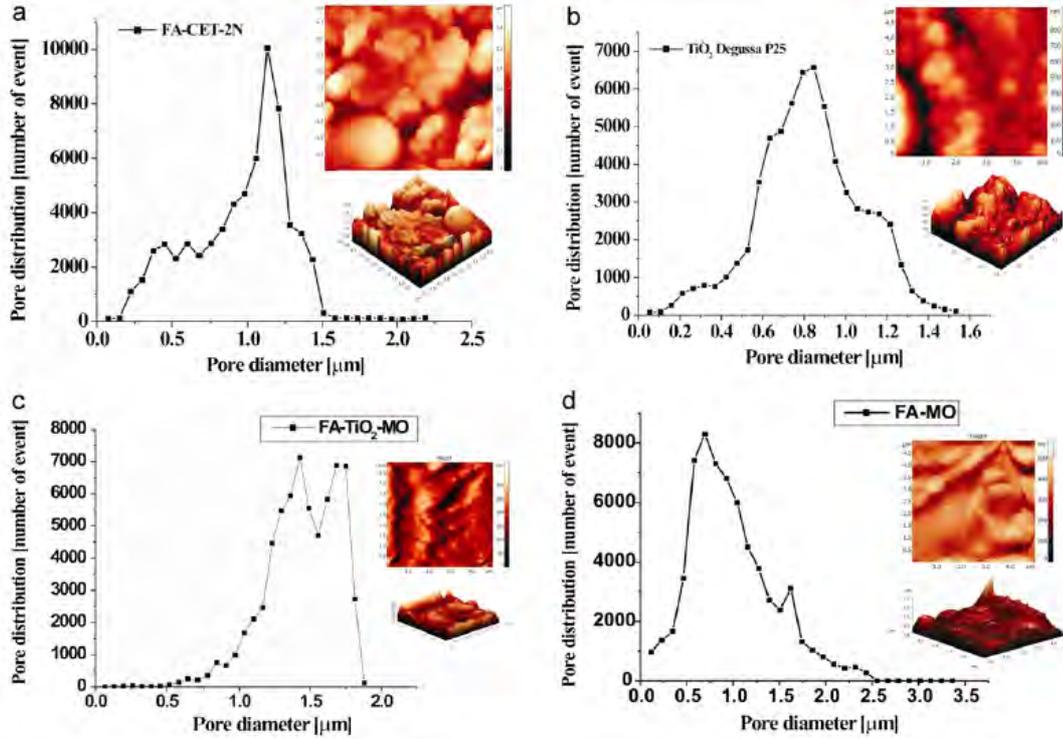
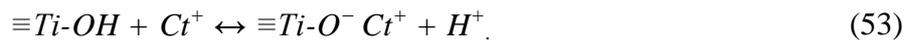


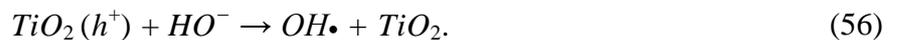
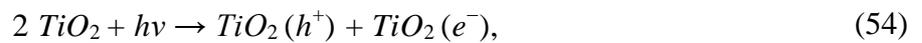
Fig. 74. The AFM topography and average macro-pore size distribution in: a) FA-M before adsorption; b) TiO_2 before adsorption; c) FA+ TiO_2 after MO interaction; d) FA-M after MO adsorption [257]

Large pores are developed as result of particle aggregation. It is interesting to notice that MO adsorption uniformly fills the FA-M voids, thus shifting the distribution maxima to lower values, while the dye adsorption on the mixed substrate results in higher maxima for TiO_2 , proving preferential adsorption.

Adsorption:

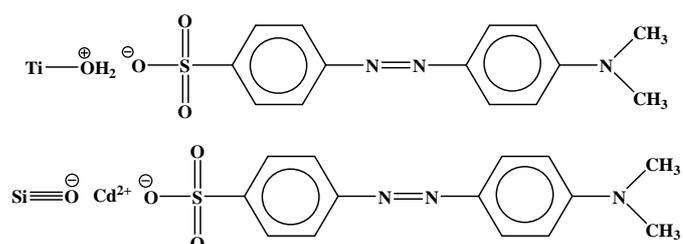


Photocatalysis:



The TiO_2 based compounds on the FA-M surface are expected to host similar processes.

On the FA-M: TiO_2 mixture, simultaneous processes of adsorption and photocatalysis will be developed. A competition is expected on the active sites, but dyes adsorption is less favored considering the working pH ($\text{pK}_{\text{aMO}} = 3.7$) when the ionized form has a negatively charged head. These processes can be; dyes adsorption on the heterogeneous mixture FA-M: TiO_2 surface, according to Eqs.:



The results presented in Fig. 75a prove that, without H_2O_2 addition a change in the mechanisms is registered after 180 min; this can be possible the result of a slow, in situ Fenton type process, caused by the Fe^{2+} and Mn^{3+} , on/near the surface of the fly ash.

Under UV irradiation, the effect of H_2O_2 is much stronger Fig. 75 and the efficiency strongly increases, although the changes in the slopes may indicate various mechanisms or various pore sizes/reaction sites opened to adsorption/photo-degradation.

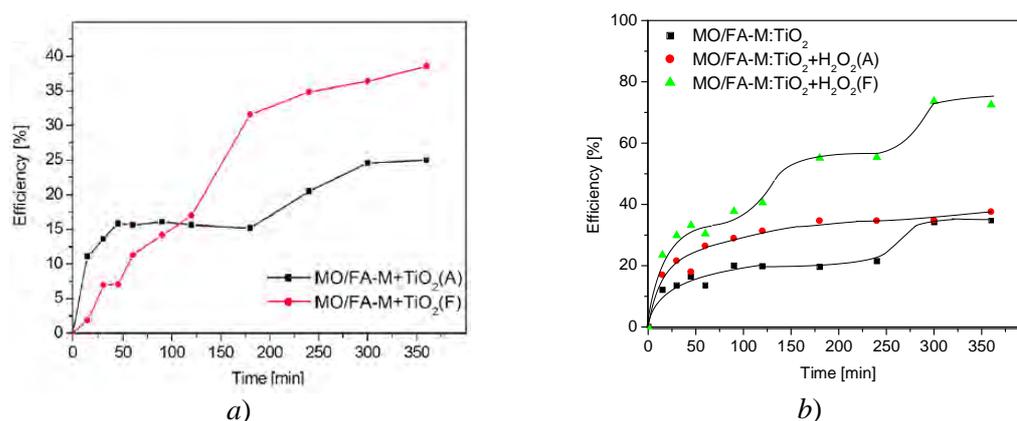


Fig. 75. Methyl-orange removal efficiency on FA: TiO_2 substrates without H_2O_2 (a) and with H_2O_2 under visible light (A) and under UV irradiation (F) [259]

The concentration of the dye represents another parameter of interest. According to the data presented in Fig. 75b, higher removal efficiencies correspond to the lower concentration (C_2), both in adsorption and in photodegradation. The slopes variation indicates that initial

processes are followed by concurrent reactions, as result of new species generated in the H_2O_2 reaction with the oxides from the fly ash. Considering these results the optimized MO removal conditions from single component solutions are: a dye concentration of $5 \times 10^{-5} \text{ mol L}^{-1}$, using a mixed FA-M:TiO₂ substrate, with a contact time of 300 min, when H_2O_2 is added, under UV irradiation when efficiencies over 90% can be reached. Efficiencies up to 70% can be reached in similar conditions in environmental conditions.

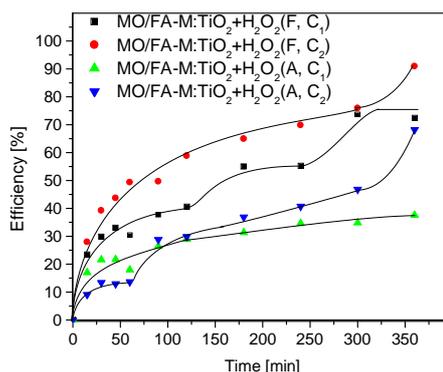


Fig. 76. Methyl-orange removal efficiency on FA-M:TiO₂ substrates from monocomponent pollutant systems in adsorption (A) and photocatalytic (F) experiments: influence of H_2O_2 addition and (b) influence of the MO concentration ($C_1 = 10^{-4} \text{ mol L}^{-1}$ and $C_2 = 5 \times 10^{-5} \text{ mol L}^{-1}$)

Under UV irradiation, the mixed substrates of modified fly ash and TiO₂ proved to be highly efficient in methyl-orange could be well removed, with efficiencies above 75% (after 300 min), when H_2O_2 was added to systems with the dye concentration of 0.05 mM.

Wood fly ash is other substrate favorite for dyes especially for MB, Fig. 77. As the results show, the MB has a higher affinity for wood ash, is more efficient in MB adsorption than heavy metal.

This can be caused by at least to factors: a higher negative surface charge of WA-W and/or larger pores (and, consequently, lower specific surface) of FA-W.

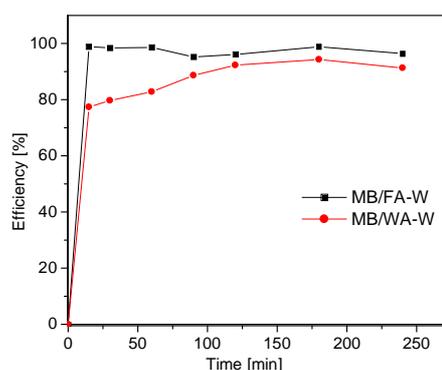
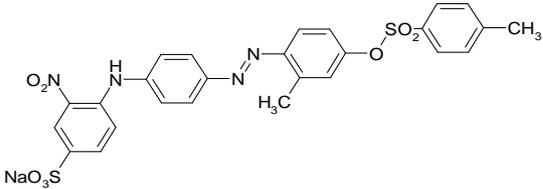
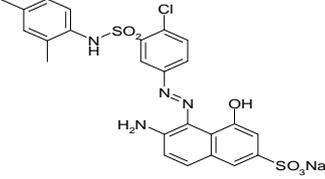
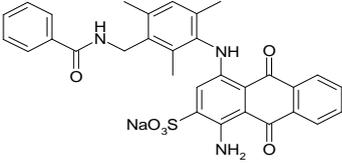
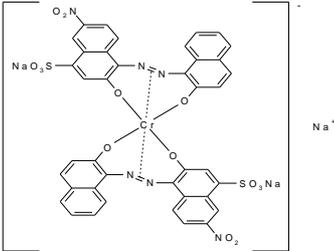


Fig. 77. Time influence on the MB adsorption efficiency ($c = 1.5 \text{ mMol/L}$) from single pollutant solutions [242]

High efficiencies, over 90% were obtained when using wood fly ash, from single pollutant systems, in parallel adsorption processes.

Further investigations were done on industrial wastewaters, loaded with three dyes presented in Table 35.

Table 35. Industrial dyes and their chemical structure

Dye	Structure	Chromophore Groupe
Bemacid Gelb N-TF (BG)		Azo
Bemacid Rot N-TF (BR)		Azo
Bemacid Blau N-TF (BB)		Anthraquinone
Bemaplex Schwarz D-R (BS)		Metal-complex

Adsorption on modified fly-ash and FA+TiO₂, substrates is discussed as a possible alternative to the industrial processes used for the treatment of wastewaters resulted in the dye finishing industry [167].

Two dyeing compositions are used for polyamide fabrics, containing three dyes and one leveling agent, Table 36.

Sarabid C14 is a reactive dye-bath conditioner, promoting levelness and increasing the dyestuff solubility while decreasing dye clustering. It is based on a polyacrylate - anionic dispersant mixture.

Table 36. Dying bath composition

Recipe	Composition [%]				
	Bermacid Gelb N-TF*	Bermacid Rot N-TF*	Bermacid Blau N-TF*	Bemaplex Schwarz D-R*	Sarabid C14**
R1 (black)	0.25	0.2	0	4	0.2
R2 (bronze)	0.23	0.13	0.17	0	0.2

*Producer: Bezema AG, Switzerland; **Producer: CHT, India.

Wastewater samples were collected from the SC MAGNUM SX textile company, Romania as follows:

- Sample 1 from the dying bath using R1;
- Sample 2 from the dying bath using R2;
- Sample 3 from the rinsing bath, following the dying bath using R2.

Adsorption on fly ash was comparatively discussed with adsorption and photocatalysis, both on fly ash and a mixed suspension with TiO₂.

Based on the above mentioned results, adsorption tests were done, aiming to increase the dye removal efficiency and to elucidate the kinetics.

Experiments were designed to investigate:

- I. the FA adsorption under visible light;
- II. the FA adsorption and photocatalytic effect under UV (possible Photo-Fenton reactions due to the iron ions);
- III. the FA + TiO₂ adsorption and photocatalytic effect under UV.

The analysis of the UV-VIS absorbance spectra showed that, in every situation the peak at the lowest wavelength has the fastest decay in time therefore all the calculations were done considering it. This (surprisingly) indicates that the more flexible dye molecules (BG and BR) adsorb slower than the rigid ones (BS and BB), probably due to a convenient amount and distribution of the accessible active sites.

The adsorption efficiencies are presented in Fig. 78.

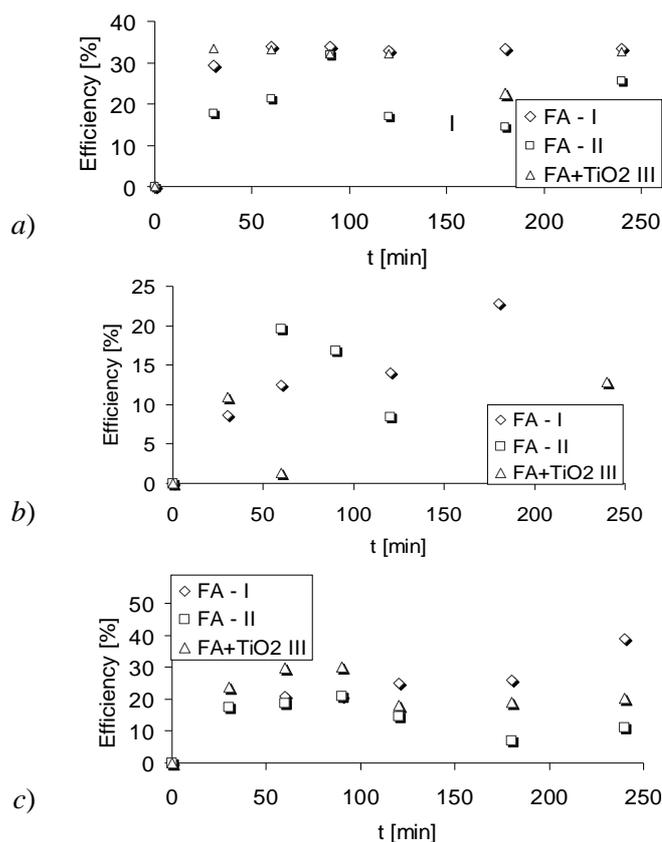


Fig. 78. Adsorption (I) and adsorption and photocatalysis (II, III) efficiencies for: a) Sample 1; b) Sample 2 and c) Sample 3

The highest adsorption efficiency on FA is registered for Sample 3, with much lower dye content, as resulting from rinsing. Corroborating these data with those presented in Table 37 we conclude that the high COD and CBO₅ values after adsorption are mainly resulting from the conditioner (Sarabid C14), which absorbs in IR and is poorly adsorbed.

Table 37. Properties of wastewater before and after treatment ($t_{\text{adsorption}} = 120 \text{ min}$)

Sample		pH	TDS [mg/L]	BOD ₅ [mgO ₂ /L]	COD [mgO ₂ /L]	TOC [mg/L]	Color [deg]	Cr [mg/g]
Sample 1	Raw	3.52	1404	2625	3406	1820	8	1.35
	Treated	6.50	1520	1252	2390	1190	0.410	0.41
	%	-	-8.2	52.3	29.8	34.6	94.9	69.6
Sample 2	Raw	5.67	824	2095	3962	1920	1	0
	Treated	6.93	896	1012	1820	1060	0	0
	%	-	-8.7	51.7	54.1	44.9	100	-
Sample 3	Raw	6.07	440	1002	1220	907	1	0
	Treated	7.66	396	610	620	420	0	0
	%	-	10	39.1	49.2	53.7	100	-
<i>Discharge limits</i>		5-9	100	40	120	-	*)	0.05

*) not objectionable

Large variations are registered during dyes' adsorption. In Sample 1, with a high metal-complex concentration, a rather high and constant efficiency is obtained even after 30 min. suggesting mono-layer adsorption of BS. The correspondent values for Sample 2 and 3 show that the azo dyes are weakly adsorbed.

Adsorption under UV conditions mostly result in lower efficiencies. One possible explanation is that during dyes photocatalysis smaller by-products are formed, faster adsorbing on the substrate(s) thus occupying the active sites before the remaining dyes. Since this effect is also registered for the FA under UV irradiation we may conclude that there is a photocatalytic reaction even in the absence of TiO₂.

Different kinetic adsorption mechanisms were tested (pseudo-first order, interparticle diffusion) but only the pseudo-second order kinetics, could well model the processes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (57)$$

where k_2 the pseudo second-order rate constant of adsorption.

The kinetic parameters were calculated and are presented in Table 38.

Beyond these, complex mechanisms of adsorption/desorption are likely and a single model cannot describe the mechanism.

Table 38. *The kinetic parameters*

Sample	FA				FA + TiO ₂	
	Adsorption (I)		Photocatalysis (II)		Photocatalysis (III)	
	q _e [mg/g]	k ₂ [g/mg min]	q _e [mg/g]	k ₂ [g/mg min]	q _e [mg/g]	k ₂ [g/mg min]
Sample 1	42.19	0.015	32.57	0.002	68.96	0.002
	t = 0-240 min; R ² = 0.999		t = 0-240 min; R ² = 0.892		t = 0-240 min; R ² = 0.979	
Sample 2	6.99	0.005	-	-	5.33	0.029
	t = 0-120 min; R ² = 0.994		-		t = 0-240 min; R ² = 0.946	
Sample 3	6.88	0.001	6.78	0.004	8.89	0.009
	t = 0-240 min; R ² = 0.899		t = 0-120 min; R ² = 0.990		t = 0-90 min; R ² = 0.995	

The pseudo-second order kinetic mechanism implies an amount of active sites of the same order of magnitude as the adsorbed species.

As calculated on the UV-VIS spectra, these data show a fast adsorption of the metal-complex dye on FA (Sample 1); the decreased rate constants values under UV irradiation confirm the modifications in the adsorption system. The maximum uptake, higher on the substrate also containing TiO_2 shows that, for the systems containing BS, the most affected by the adsorption of small molecules is the FA.

Significant differences were registered in the kinetic parameters for Sample 2 and Sample 3. Although the maximum uptake is similar (same dye components) the rate constants differ as result of the non-dye content. One assumption is that rinsing could mainly act upon Sarabid C14, increasing its concentration comparing to the dyestuff, thus making him part of the competitive adsorption. The higher k_2 values on TiO_2 +FA mixtures prove that photodegradation is a rather fast process in the absence of heavy metals, and occurs on a limited amount of active.

The adsorption kinetic was investigated on modified fly ash as single substrate and on mixed suspensions with TiO_2 .

The studies allow the calculation of the dyes removal efficiency and of the kinetic parameters, for the pseudo-second order mechanism. The results show that, in designing an industrial wastewater treatment process, results obtained on single-dye solutions must be completed with data specifically obtained on real wastewaters. Competitive adsorption occurs between the initial components and between these and possible by-products resulted after photocatalysis.

IV. Fly Ash Based Substrates for Heavy Metals and Dyes Removal in Simultaneous Adsorption and Photocatalysis Processes [251, 260]

IV.1. Alkali Modified Fly Ash for Simultaneous Removal of Mixtures Containing one Heavy Metal and one Dye

In designing a single step process, it is important to identify the reciprocal influences of all the components (cadmium, copper and methyl orange) on the final efficiency.

The following adsorption experiments were carried and then discussed as tailoring tools for high efficient processes using alkali modified fly ash, FA/NaOH 2N.

The tests were done by adding 2 g of substrate to 100 mL solution of:

- a) Cd^{2+} + MO 0.025 mmol/L;
- b) Cu^{2+} + MO 0.025 mmol/L.

The mixture was stirred up to 90 min at room temperature, then the substrate was removed by vacuum filtration and the supernatant was analyzed: heavy metals concentration was measured using AAS while MO quantitative analysis was done by UV-VIS spectroscopy at $\lambda_{\text{max}} = 464 \text{ nm}$.

The results presented in Fig. 79 show good removal efficiencies, both for heavy metals and the MO also has good adsorption efficiency and does not interfere with the heavy metal adsorption.

The adsorption efficiency, η , was evaluated based on the initial and equilibrium absorbance ($A_{\text{MO}}^i, A_{\text{MO}}^e$) for MO:

$$\eta = \frac{A_0 - A}{A_0} \cdot 100. \quad (58)$$

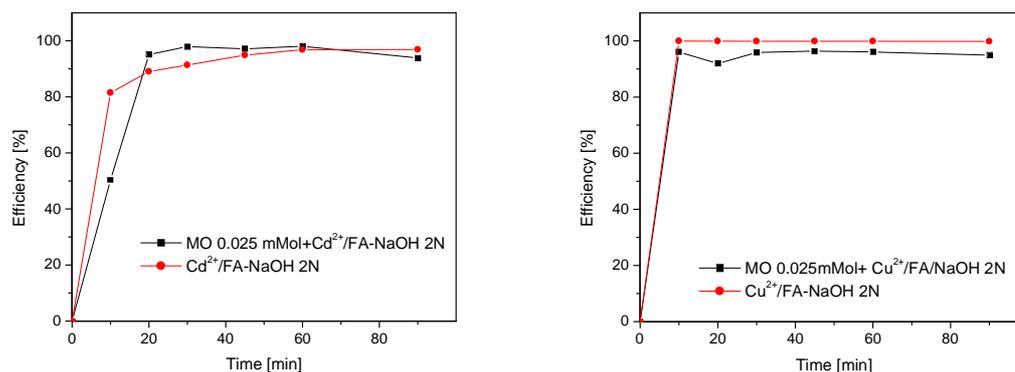


Fig. 79. Adsorption efficiency vs. contact time

The pseudo-second order rate equation can well describe the adsorption in all the experimental tests, Table 39, MO present in solution can be adsorption on fly ash involving new active sites increasing affinity for heavy metals. An increase in the substrate capacity was registered in solutions also containing MO, supporting the assumption of dye's bonding on the FA surface.

Table 39. The kinetic constants of pseudo-second order kinetic [260]

System	k_2 [g/mg min]	q_e [mg/g]	R^2
Cd²⁺/FA-NaOH 2N	0.114	12.755	0.999
Cd²⁺ + Methyl Orange/FA-NaOH 2N	0.097	16.921	0.999
Cu²⁺/FA-NaOH 2N	0.005	4.866	1
Cu²⁺ + Methyl Orange/FA-NaOH 2N	0.105	14.880	0.999

The reaction rates in system containing MO are almost constant (0.1 g/mg min), as consequence of the uniform surface resulted from the dye adsorption on FA.

Further experiments were designed for systems also involving methylene blue. Experiments were designed for the simultaneous removal of heavy metals and dyes, using a composite powder of fly ash and activated carbon. The results show that adding a small amount of activated carbon, in a powder mixture with modified fly ash is highly effective in removing HM and dyes (Methylen blue or methyl orange) from wastewater.

Three series of tests were done, on solutions containing:

- (1) CdCl₂;
- (2) CdCl₂ with Methylen blue (MB, C₁₆H₁₈ClN₃S);
- (3) CdCl₂ with methyl orange (MO, C₁₄H₁₄N₃SO₃Na).

The interactions between the dye and FA depend on the surface charge of the substrate (predominant negative) and on the dye molecular structure. These interactions could be thus controlled, by choosing the dye for a specific cation or group of cations leading to efficient, low cost substrates.

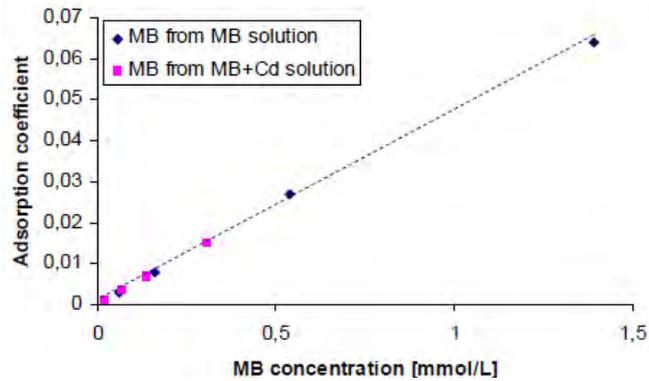


Fig. 80. Adsorption isotherms of MB [251]

Chemisorption is the likely mechanism also for MB adsorption on the FA:PAC substrate; the adsorption coefficients are much lower as result of the large volume of the dye molecule but also as a consequence of the much lower concentrations. By combining FA with photocatalysts (TiO₂) and/or adsorbents (activated carbon) a complex system, able to simultaneous treat dyes and heavy metals is obtained [227] and the experimental adsorption isotherms for cadmium and MB, are presented in Figs. 80 and 81, the Langmuir isotherm describes cadmium adsorption from mono-ionic solutions and from solutions also containing MB.

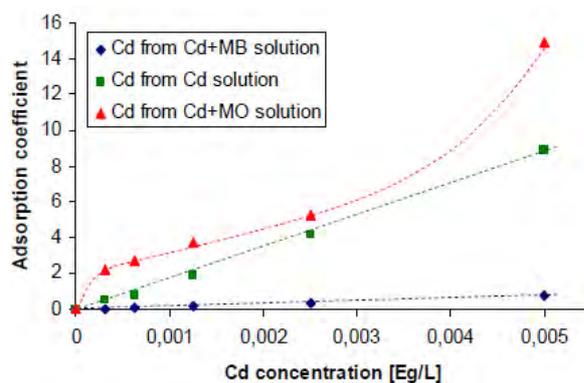


Fig. 81. Adsorption isotherms of Cd²⁺ (a) and MB (b)

Thus, in designing a single step process, it is important to identify the reciprocal influences of all the components on the final efficiency Fig. 82.

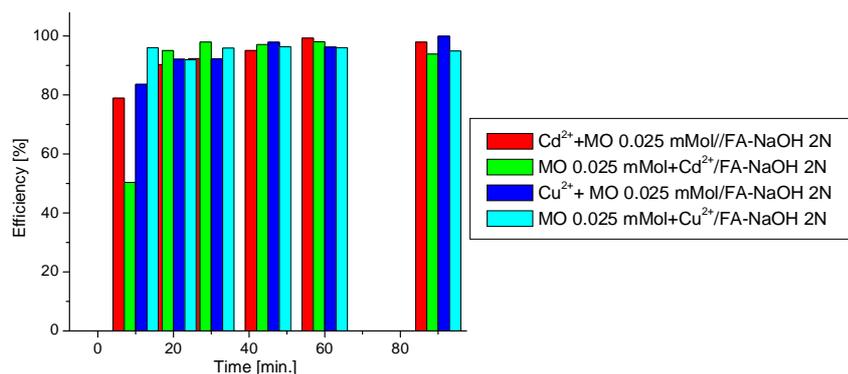


Fig. 82. The efficiency in MO and heavy metal removal

IV.2. Fly Ash Based Composites for Simultaneous Removal of Mixtures Containing one Heavy Metal and one Dye [257]

As already presented, the alkali modified fly ash can develop composites with TiO_2 , highly efficient in heavy metals removal.

Therefore, in a next step comparative studies developed on alkali modified FA and its mixture with TiO_2 were developed to identify the potential of these substrates for the simultaneous removal of a dye (methylene blue) and a heavy metal (cadmium and copper).

The FA structural and morphology analysis showed that the crystalline oxides composition can be tailored by the NaOH 2N treatment, resulting in negatively charged surfaces, with open, interconnected pores, efficient in removing both the dye and the heavy metals Figs. 83 and 84.

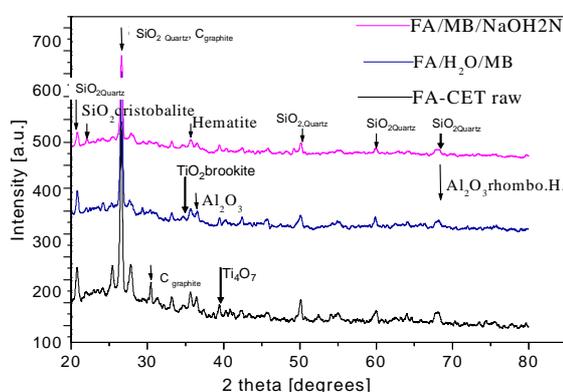


Fig. 83. XRD of raw FA and FA modified with NaOH 2N and MB

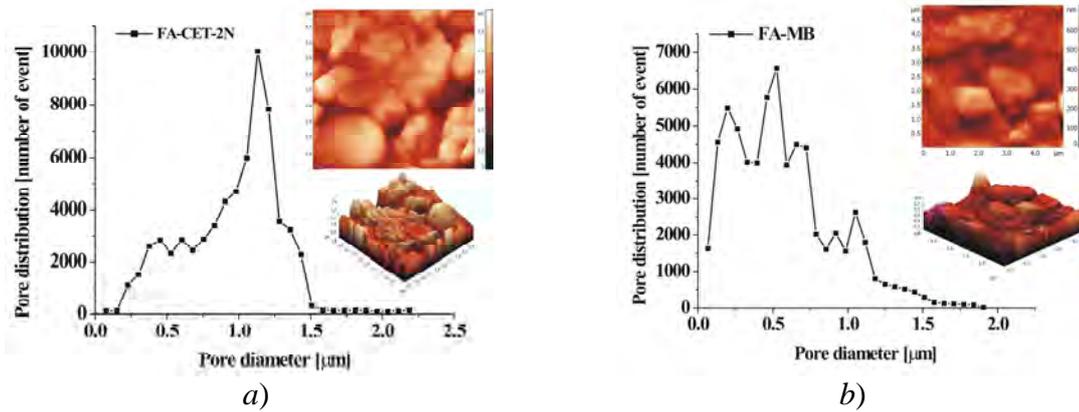


Fig. 84. The AFM topography: a) FA/NaOH 2N before adsorption; b) FA/NaOH 2N/MB

The adsorption mechanisms and the kinetic data were comparatively evaluated on two types of suspensions:

- (a) 1 g FA/NaOH 2N in 25 mL;
- (b) (0.75 g FA/NaOH 2N + 0.25 g TiO₂) in 25 mL of complex solution of CdCl₂ (Cd²⁺, 0-550 mg/L) with MB, or CuCl₂ (Cu²⁺, 0-380 mg/L) with MB.

For the kinetic studies, aliquots were taken at certain moments (up to 240 min), when stirring was briefly interrupted and, after filtration on 1.5 µm filter, the supernatant was analyzed. The efficiency is presented in Figs. 85 and 86.

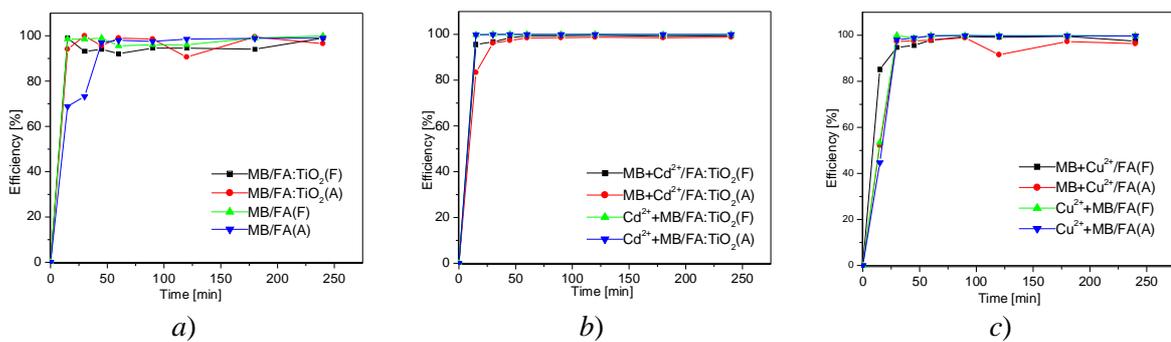


Fig. 85. Adsorption efficiency vs. time from:

- a) MB; b) Cd²⁺ +MB and c) Cu²⁺ +MB solutions [257]

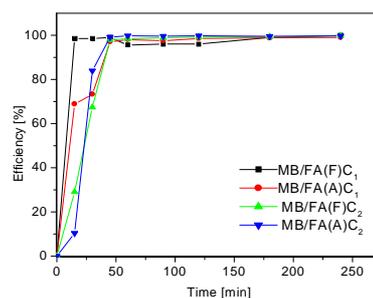


Fig. 86. Influence of the MB concentration

Table 40. Kinetic parameters of the MB adsorption (A) and photodegradation + adsorption processes (F)

Parameter	MB		MB		MB/(MB+Cu)	
	(A)	(F)	(A)	(F)	(A)	(F)
Adsorbent	FA	FA	FA+TiO ₂	FA+TiO ₂	FA+TiO ₂	FA+TiO ₂
q _e [mg/g]	0.37	0.39	0.16	0.16	0.52	0.52
k ₂ [g/mg · min]	6.20	32.52	1.40	11.60	5.53	1.28
R ²	0.999	0.979	0.998	0.998	0.996	0.999

Table 41. Kinetic parameters of the heavy metal removal

Parameter	Cd/(Cd+MB)		Cu/(Cu+MB)	
	(A)	(F)	(A)	(F)
Adsorbent	FA+TiO ₂	FA+TiO ₂	FA	FA
q _e [mg/g]	13.48	13.487	9.69	9.65
k ₂ [g/mg · min]	0.001	0.001	0.47	0.32
R ²	1	1	0.994	0.997

The maximum uptake values for MB are much lower compared to those corresponding to copper, but this does not lower the process viability since the usual concentration ratio between the dyes and the heavy metal concentration is 1:1000 in the wastewaters resulted in the textile industry. On the other hand, the rate constants are high, especially under UV irradiation as result of adsorption followed by photodegradation (Tables 40 and 41). The highest value, obtained in the FA/NaOH 2N - UV system may confirm the assumption of parallel adsorption, semiconductor photocatalysis and photo-Fenton processes, with comparable rates and with an amount of active sites comparable with the amount of species involved in the mechanisms (as the pseudo-second order kinetic defines). Copper may activate the adsorption system containing MB but the resulted complexes are slowly degraded under UV.

The MB removal from solutions also containing cadmium could be modelled using the pseudo-second order kinetics only on the 60-240 min range, with a rate constant of 0.48 g/mg · min⁻¹.

The substrates heterogeneity is high even when using FA and complex mechanisms are confirmed. The Freundlich parameters indicate various adsorption affinities of the substrate(s) for the solution components with a net superiority of the modified FA (Table 42).

Table 42. *Freundlich parameters for the heavy metals and MB adsorption from binary systems*

Parameter	Cd/(Cd+MB)		Cu/(Cu+MB)		MB/(MB+Cd)	
	FA+TiO ₂	FA	FA+TiO ₂	FA	FA+TiO ₂	FA
n	0.902	0.242	1.837	0.688	1.358	0.866
k _f	186.21	1819.70	1.20	321.07	131.13	2375.74
R ²	0.925	0.922	0.956	0.963	0.926	0.994

IV.3. Fly Ash Based Composites for Simultaneous Removal of Mixtures Containing More Heavy Metals and one Dye [226]

As industrial wastewaters have a more complex pollutants load, the next step was to further extend the studies to investigate the concurrent adsorption in systems containing two and three heavy metals and one dye. One study reported and most cited developed the effect of MB adsorbed on the fly ash surface on the removal efficiency of cadmium, copper and nickel ionic species from complex, multi-cationic dye solutions [226]. The paper studies the effect of MB adsorbed on the fly ash surface on the removal efficiency of cadmium, copper and nickel ionic species from complex, multi-cations dye solutions.

The research plan followed steps concerning the heavy metals removal from single cation (Cd²⁺, Cu²⁺, Ni²⁺) solutions [227, 228], simultaneous removal of cations from multi cations solutions using FA and FA:TiO₂ mixtures in parallel with similar studies of dyes removal via photo-degradation and adsorption. Then mixtures of single cation solutions with dye(s) were investigated for understanding the complex influence of the components on the substrates, and the changes in mechanisms and efficiencies; a group of studies targeted the results obtained in Cd²⁺ and Cu²⁺ removal, using fly ash (FA) with methyl orange modified surface and its mixtures with TiO₂ and proved that the best adsorption efficiency is registered on mixture with 25% of TiO₂ [229]. Similar studies were carried out on fly ash modified with methylene blue, MB. The efficiency was very good, both for the cations and for the dye, and a new idea was born for a complex adsorption process involving cadmium, copper and nickel ionic species from multi-cationic dye solutions.

In all experiments the initial MB concentration was fixed at 0.05 mmol/L, while the heavy metal concentration was varied up to 0.01 mol/L.

The optimal contact time was evaluated on suspensions of 2 g FA/NaOH 2N in 100 mL of equimolar multi-cation solutions of cadmium, cooper and nickel; aliquots were taken at certain moments (10, ..., 120 min), when stirring was briefly interrupted and after decantation and filtration the volumes of supernatant were analyzed. The residual metal concentration in the aqueous solution was analysed by AAS, and the MB concentration was evaluated by UV-VIS spectrometry, on the calibration curve registered at the maximum absorption wave length ($\lambda_{MB} = 664$ nm).

These chemical and structural changes are mirrored in morphology modifications, resulting in large differences in the substrates' affinity for heavy metals and dyes. The various pore size distributions and morphologies, Fig. 87, appear due to leaching of the alkaline and alumina oxides followed by the formation of new structures with important role in the heavy metals and MB adsorption.

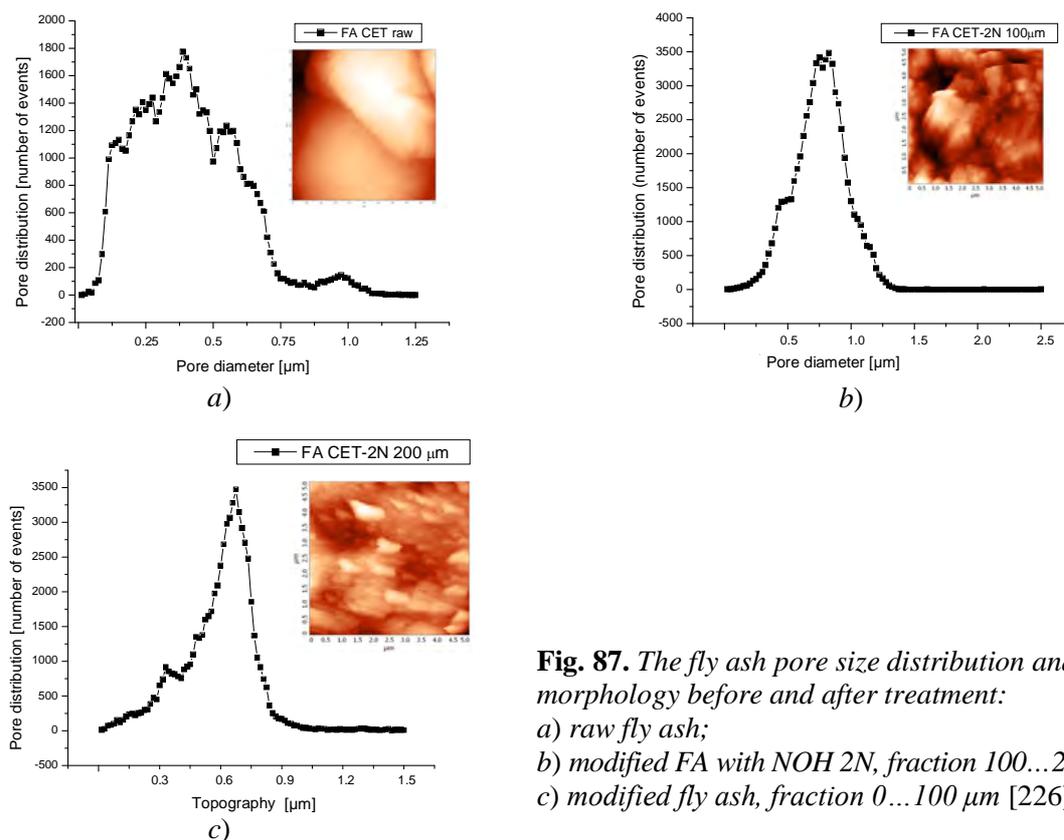


Fig. 87. The fly ash pore size distribution and morphology before and after treatment:
 a) raw fly ash;
 b) modified FA with NOH 2N, fraction 100...200 μm;
 c) modified fly ash, fraction 0...100 μm [226]

The effect of the contact time on the efficiency of the heavy metal adsorption and MB is presented in Fig. 88a-d.

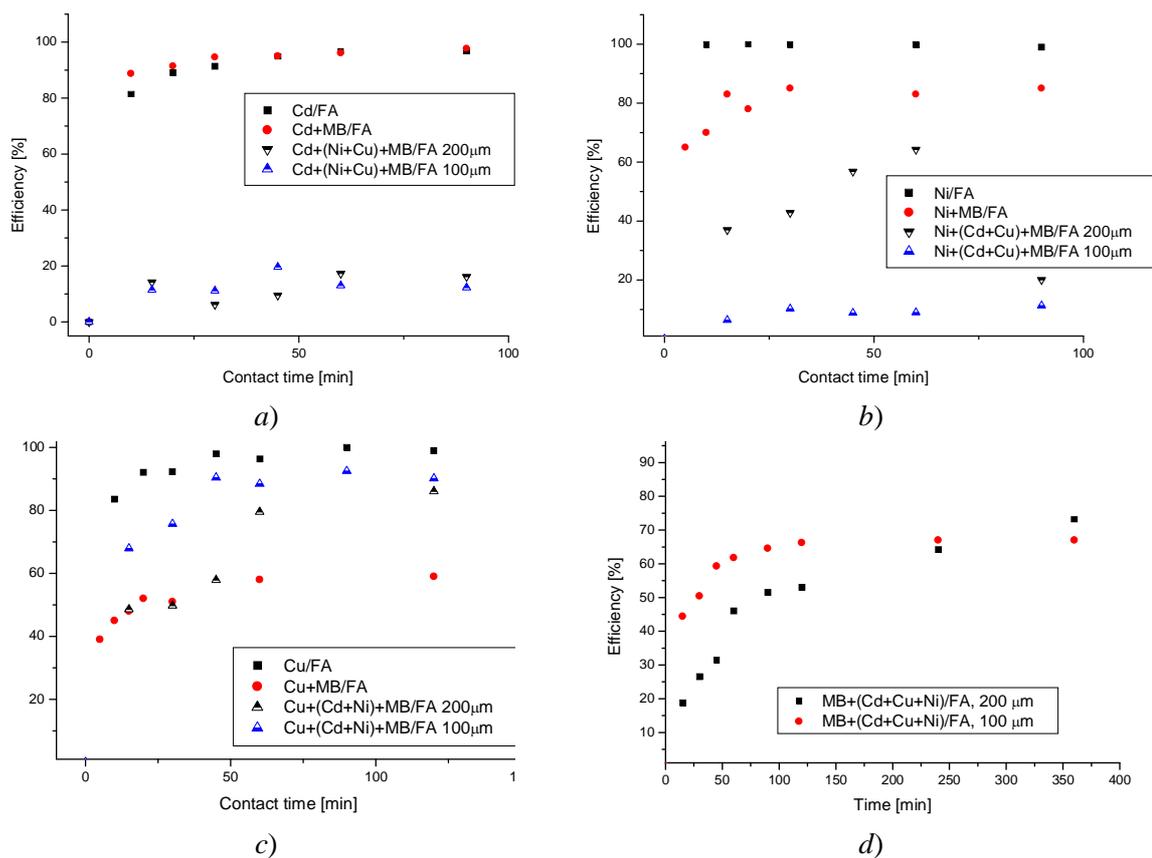


Fig. 88. Time influence on the adsorption efficiency from mixed solutions, for: a) cadmium; b) nickel; c) copper; d) methylene blue

Single component solutions, containing only one heavy metal cation can be well treated using modified FA even with a contact time of 30 min or less. This recommends the mixed (100 μ m + 200 μ m) modified FA substrate as appropriate for up-scaling.

Two component solutions of heavy metal and dye have different adsorption efficiencies as result of two possible effects: (1) cation complexing, resulting in larger volume specie(s), thus with lower diffusion rate towards the substrate, and/or (2) competitive adsorption between the cation species and the dye. In the first case longer contact durations would result in significant increase in the adsorption efficiency, which was not registered. The second effect has a higher likelihood and can suggest an affinity order of the species, toward the substrate: Cd > Ni > MB > Cu.

Multi component solutions, containing the three heavy metals in equimolar ratio and MB have a complex adsorption mechanism, with competitions among the heavy metals and among these and the dye; the much lower efficiencies registered for cadmium and nickel can be the result of a competitive adsorption mainly among these two cations, having similar hydrated volume, with a small advantage for nickel.

The strong increase in copper adsorption efficiency can be explained considering the highest MB affinity for the substrate; based on the results one can say that the dye is firstly adsorbed on the substrate and then copper is adsorbed on this new layer, with good efficiency. The highest values registered in copper adsorption after 60 min (Fig. 88c) can be corroborated with the substrate saturation with MB (Fig. 88d). The larger affinity of the FA/MB substrate for copper can also be the result of the smaller volume of copper, due to a lower hydration number. In aqueous media, heavy metals cations exist as hydrated complexes with different number of water molecules. The ionic radii of the dehydrated and hydrated species are presented in Table 43, along with the hydration numbers for cadmium, copper and nickel. The hydrated structure of the Cu (II) ion has been a subject of ongoing debate in the literature. Recent results [234] show that aqueous copper structures include not only 4...6 water molecules hydrated complexes but also clusters, containing up to 14 water molecules. Still, the slightly acid environment (working pH of 4.8...5.3) is responsible for low water coordination of copper, resulting in aqua-complexes with lower volume and higher mobility, comparing to cadmium and nickel [235].

Table 43. *Properties of the dehydrated and hydrated heavy metal cations*

Heavy metal	Cadmium	Nickel	Copper
Dehydrated ionic radius [nm]	0.097	0.072	0.072
Hydration number	6	6	4...6
Hydrated ionic radius [nm]	0.426	0.425	0.295

The data also show that the hydrated cadmium and nickel have a much lower affinity for the FA/MB substrate, showing for nickel actually an efficiency decrease for longer contact times, of 120 min (Fig. 88b). This can also be linked with the higher hydration number (and lower ionic degree) of these two cations. The results confirm the need for optimising the process parameters if industrial applications are targeted.

The substrate influences the adsorption process not only through its composition but also through the porosity. The 200 μm FA fraction, with narrow pore size distribution and a maximum pore diameter of 746 nm leads to better adsorption efficiencies both for cadmium and nickel. The 100 μm fraction has smaller grains, with a broader pore distribution, centred on 842 nm, mainly as result of the initial composition, containing predominantly soluble oxides, with lower mechanical strength. On this substrate, copper reaches adsorption

efficiencies of 90% after 45 min., values obtained on the 200 μm fraction only after 120 min of contact time. The results can lead to the conclusion that, in the defined experimental conditions, the most important factor is the substrate’s composition, corroborate with the heavy metal cation type and hydration.

The heavy metal adsorption could well be described by the Langmuir model [159].

The monolayer adsorption fits well with the efficiency data that show saturation after a rather limited contact time (during these experiments the contact time was set at 60 min). The Langmuir parameters are presented in Table 44.

Table 44. Langmuir parameters for the heavy metals adsorption from multicomponent systems

	Cu/(Cd+Cu+Ni+MB)		Cd/(Cd+Cu+Ni+MB)		Ni/(Cd+Cu+Ni+MB)	
FA Fraction	100 μm	200 μm	100 μm	200 μm	100 μm	200 μm
q _m [mg/g]	12.78	10.18	6.36	3.77	1.25	1.66
a [L/mg]	0.004	0.012	0.010	0.404	0.721	0.094
R ²	0.997	0.997	0.999	0.983	0.998	0.999

Similar efficiency variations are obtained on both types of substrates: FA/NaOH 2N 100 μm and 200 μm, proving that the surface composition and charge play a key role and that morphology/porosity is of secondary importance.

High adsorption efficiencies are registered for Cd²⁺, Cu²⁺, Ni²⁺ and MB concentrations up to 0.001 mol/L on FA/NaOH 2N for 100 and 200 μm size as Fig. 89a and 89b show.

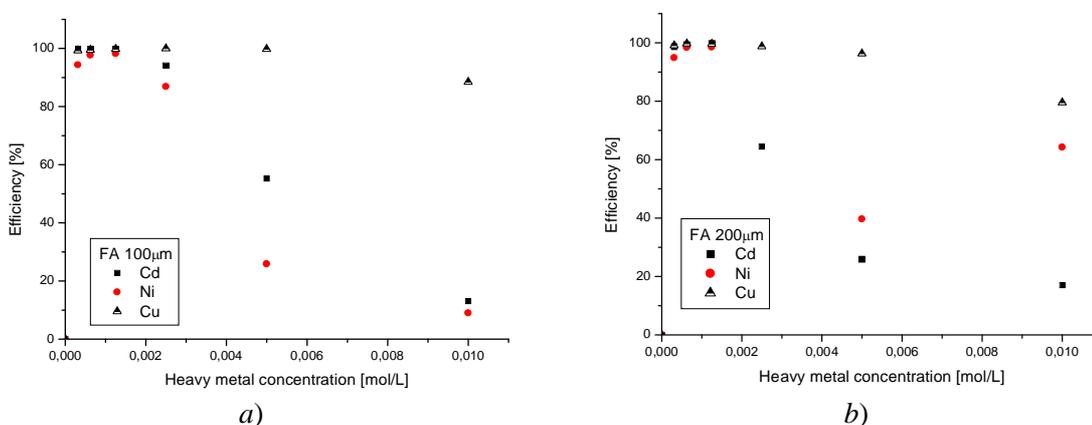


Fig. 89. Concentration influence on the adsorption efficiency on FA fractions: a) 100 μm; b) 200 μm

Based on the linearization of the equation developed by Ho and McKay the pseudo-second order kinetic parameters were calculated and are presented in Table 45.

Table 45. Kinetic parameters of the heavy metal adsorption

Parameter	Cu/(Cd+Ni+Cu+MB)		Cd/(Cd+Ni+Cu+MB)		Ni/(Cd+Ni+Cu+MB)	
	FA-100 μm	FA-200 μm	FA-100 μm	FA-200 μm	FA-100 μm	FA-200 μm
q_e [mg/g]	13.2	11.3	3.7	3.8	1.6	2.6
k_2 [g/mg · min]	0.247	1.176	0.556	5.194	4.224	0.309
R^2	0.996	0.995	0.889	0.966	0.958	0.957

The maximum adsorption capacity, evaluated based on the Langmuir model and using the pseudo-second order kinetic have close values. The data show large adsorption capacity, in the experimental conditions, for the copper ion. Another important finding is that copper adsorption is rather slow comparing to cadmium thus good efficiencies can be reached only at rather long contact times. The results confirm that both FA fractions have almost the same affinity, thus sieving is actually not necessary.

Based on these results following conclusions could be outlined, as a step forward in the design of adsorption systems for the simultaneous removal of heavy metals and dyes:

1. Simultaneous removal of the methylen blue dye and cadmium, copper and nickel is possible on fly ash modified with NaOH 2N. A contact time of 60 min is convenient for reaching the maximum efficiencies.
2. The dye adsorbs on FA and, on this new surface copper exhibits a higher affinity for the active sites comparing to cadmium and nickel. The reason may be the higher mobility and ionic degree of the copper tetra-hydrated complex, comparing to the hexa-complexes of Cd and Ni, at the working pH of 4.8...5.3.
3. The efficiency of the heavy metal adsorption does not depend on the FA fraction used. This becomes significant for the adsorption of large molecules, as it is MB.
4. The pseudo-second order kinetics describes well all the processes. Large adsorption capacities are registered for copper, confirming its higher affinity for the substrate.

5. High adsorption efficiencies are registered for heavy metals concentrations up to 0.01 mol/L, recommending the FA substrate for simultaneous removal of heavy metals and MB from wastewater resulted in the dyes finishing industry.

6. Further combination of this substrate with a photocatalyst can reach full removal of the dye.

Replacing the MB dye with MO lead to even higher adsorption affinity, described by BETT isotherm type H.

The interactions between the dye and FA depends on the surface charge of the substrate (predominant negative, as previously reported [228]) and on the dye molecular structure.

Their effect on the heavy metal removal efficiency depends on the dye - heavy metal cation interaction, most likely a complexation reaction. These interactions could be thus controlled, by choosing the dye for a specific cation or group of cations leading to efficient, low cost substrates.

IV.4. Fly Ash - TiO₂ Photo-Fenton Systems [259]

Modified fly ash (FA) mixed with TiO₂ photocatalyst represent a viable option for simultaneous removal of dyes and heavy metals from wastewaters containing methyl-orange with a remarkable stability to photo-degradation (due to the extended π -electrons delocalisation on the two aromatic rings and the adjacent groups), being therefore used as standard in many studies, and cadmium the most bio-toxic heavy metal also being mutagenic to human. For a cost-effective dye removal process, further tests were done, replacing the photocatalyst with a (photo) Fenton system.

The optimized technological parameters (contact time, amount of fly ash, and amount of Fenton systems, usually based on Fe²⁺/H₂O₂) [261] allow reaching removal efficiencies up to 88% for the heavy metal and up to 70% for the dye.

Modified fly ash (FA-M)/FANaOH 2N was selected by mechanical sieving (Analysette 3 Spartan). The 40...100 μm fraction represents 37.35%wt of the total FA and the rest of the ash could be further valorised in obtaining geo-polymers, in manufacturing concrete, bricks and ceramic tiles, or as filler in plastics and paints.

This fraction was selected because of two main reasons: (1) as adsorbent, a large specific surface is required (corresponding to low dimensional grains) and (b) these values still make possible up-scalable separation processes in designing the wastewater treatment process. The last reason also made us not to further mill this fraction.

Batch adsorption experiments were done at room temperature, under mechanical stirring (100 rpm) of suspension with the substrate FA-M; the pollutants system was bi-component solutions of MO ($C_1 = 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) + Cd²⁺ ($C_1 = 5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$); the Fenton system: FeSO₄ + H₂O₂. The iron salt (FeSO₄ · 7 H₂O), was added to reach final concentrations in the tested systems in the range $5 \cdot 10^{-4} \dots 3 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. The volume of H₂O₂ was kept constant at 50 μL resulting in a concentration of $4.45 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ in the pollutants' solutions.

In the kinetic studies, aliquots were taken at preset moments (up to 360 min), when stirring was briefly interrupted and, after filtration on a 1.5 μm filter, the supernatant was analyzed.

Preliminary experiments allowed optimizing the filter type, considering three conditions: (1) no retention of the soluble species, especially MO and Cd, to avoid results denaturation; (2) full retention of the substrates; (3) filtering rate as fast as possible, having in view the possible up-scaling.

In all experiments the solutions were tested at their natural pH. The pH value of the MO solutions in contact with FA-M was 8.6 and in contact with the mixed system FA-M + TiO₂, the pH value was 8.1, and these values are below those indicated in the Pourbaix diagram for Cd(OH)⁺ (pH = 9.2) or Cd(OH)₂ (pH > 9.5) formation at the working temperature [262].

Adding cadmium cations in the MO solutions did not alter these pH values and there was no evidence of hydroxide precipitation (as result of the low heavy metal concentrations).

In all the experiments a constant ratio substrate mass : solution volume was set at 4 g (FA: TiO₂ = 3: 1) : 100 mL.

The pollutant systems were synthetically prepared using cadmium from solid salts CdCl₂ · 2.5 · H₂O and reagent grade (C₁₄H₁₄N₃NaO₃S, Sodium4-[(4-dimethylamino) phenyldiazenyl] benzenesulfonate, dissolved in ultra-pure water.

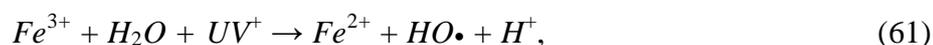
In this case, three mechanisms can be expected in the system containing both, fly ash and TiO₂: simultaneous adsorption (FA), with homogeneous (Fenton) and heterogeneous (TiO₂ and FA) photocatalysis.

The use of TiO₂ mixed with FA proved to be efficient but TiO₂ nanoparticles have quite high costs and raise technological problems in removing the photocatalyst in industrial processes. Therefore, further investigations were done to test an alternative process, based on FA and photo-Fenton system.

Photocatalysis is enhanced by a larger amount of hydroxyl radicals. One way to produce them is using Fenton systems (H₂O₂/Fe²⁺/Fe³⁺), when the oxidation-reduction process is:



Under UV irradiation, in the photo-Fenton system, supplementary amounts of $HO\cdot$ are produced from the fast hydrogen peroxide decomposition:



Besides these reactions, since FA also contains about 1% of TiO_2 , photocatalysis may also be expected. Experiments targeted the optimization of the Fe^{2+} concentration in the system containing cadmium and MO, Fig. 90.

The data presented in Fig. 90 show a higher efficiency under UV irradiation, not as result of a direct influence of the heavy metal cation, but as a consequence of faster dye degradation, thus leaving empty a larger amount of active sites for cadmium bonding onto the substrate.

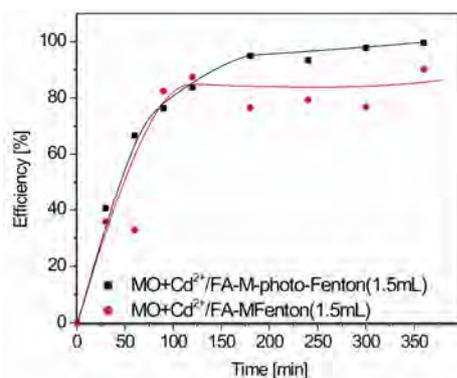


Fig. 90. Cadmium adsorption efficiency in the optimized Fenton systems

The adsorption mechanisms and the process kinetic are discussed, also considering the possibility of in-situ generation of the Fenton system, due to the fly ash composition.

Further kinetic investigations on the FA-M - photo-Fenton were developed to elucidate the process mechanism(s).

According to the specific surface data, Table 46, FA-M can be described as a meso-porous substrate and TiO_2 has rather large open pores, easily accessible to adsorption, therefore, in the experimental condition (high substrate:volume ratio), inter-particle diffusion is not likely to be the limiting factor. Different kinetic adsorption mechanisms were tested (pseudo-first

order, interparticle diffusion, Langmuir-Hinshelwood) and the pseudo-second order kinetics was found to best model the general processes.

Table 46. *The surface characteristics*

Component	Surface area [m ² /g]	Total pore volume [cm ³ /g]	Average pore diameter [nm]
FA-M	11.33	0.06	20.33
TiO ₂	54.02	0.25	30.08

Based on the linear form of the equation pseudo-second order kinetics, the kinetic parameters were calculated and are presented in Table 47 for cadmium adsorption, from bi-component solutions.

The data allow us to conclude that the amount of active sites and the amount of reactive species are comparable, in terms of adsorption.

The cadmium adsorption kinetic is moderate but the maximum capacity is high, recommending the substrate for industrial processes.

Table 47. *Kinetic parameters of the Cd²⁺ removal in photo-Fenton + adsorption processes*

Parameter	Cd ²⁺ (Cd ²⁺ + MO) C _{Fe2+} = 3 · 10 ⁻³ mol · L ⁻¹		Cd ²⁺ (Cd ²⁺ + MO) C _{Fe2+} = 2 · 10 ⁻³ mol · L ⁻¹	
	UV	Visible	UV	Visible
q _e [mg · g ⁻¹]	632.981	727.517	538.331	540.355
k ₂ [g · mg ⁻¹ · min ⁻¹]	1.575	2.838	0.002	0.009
R ²	0.978	0.973	1	1

Wastewaters containing mixed cadmium-MO can be treated using modified fly ash and photo-Fenton systems, under UV irradiation. The results allow optimizing the Fe²⁺ amount for reaching (after 90 min) methyl-orange removal efficiencies close to 70% while the cadmium adsorption was of 88%.

So in these conditions solution C₁ with H₂O₂ is recommended.

Increasing the volume of Fenton reagent the photodegradation efficiency of MO is well because the number of HO• are more several Fig. 91.

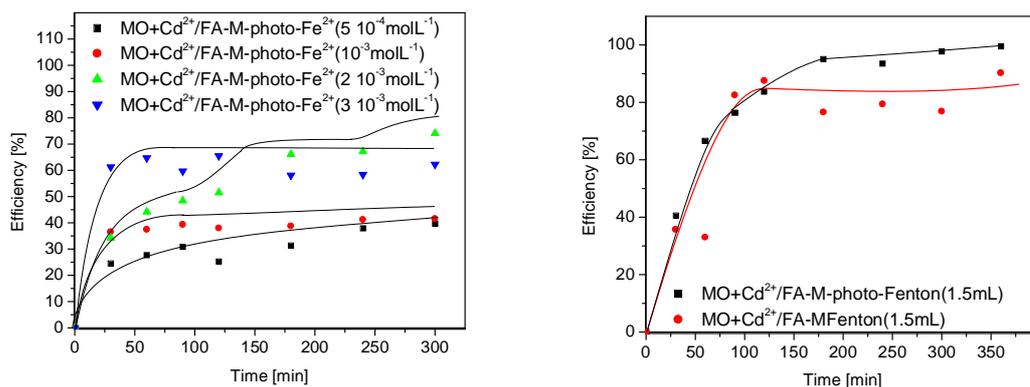


Fig. 91. Influence of the Fe^{2+} on the photodegradation efficiency of methyl-orange

The efficiency rises (in the first 120 min) proportional with Fe^{2+} concentration, Fig. 92.

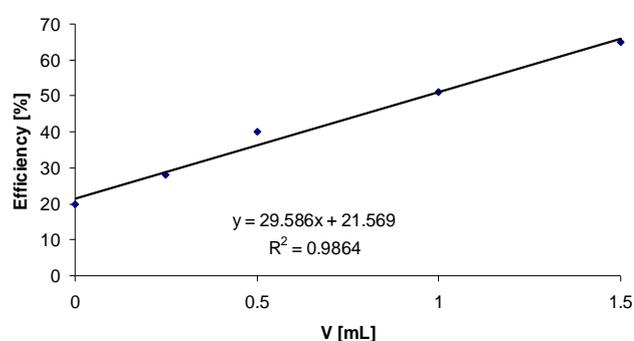


Fig. 92. Influence of the Fe^{2+} amount on the MO removal efficiency, at 90 min

Table 48. Kinetic parameters of the MO removal by photo-Fenton + adsorption (FA) processes

Parameter	MO(MO+ Cd^2)		MO(MO+ Cd^2)	
	Photo Fenton (FA+ Fe^{2+} H_2O_2) + Adsorption (FA)			
$V_{Fe^{2+}}$ [mL]	0.25	0.50	1.00	1.50
q_e [mmol/g]	0.001	0.001	0.002	0.002
k_2 [g/mg · min]	27228	5319.2	19261	4793.5
R^2	0.952	0.998	0.964	0.979

The results show that:

- at contact time 120 min (accepted technological process) can be recommended an volume of 1.5 mL Fe^{2+} 0.2N concentration. At this concentration appear a saturation equilibrium of substrate;
- when the time is longer, the efficiency increase for 1 mL Fe^{2+} , showing that intermediate degradation products can be formed, that decompose easier leaving the substrate free;
- when the volume is small ($V = 0.5$ mL) the contact time for equilibrium is longer.

As expected, cadmium is well adsorbed and irradiation does not influence the process.

The kinetic adsorption mechanisms were tested but only the pseudo-second order kinetics could describe the process, Table 49.

Table 49. Kinetic parameters of the Cd^{2+} removal by photo-Fenton + adsorption (FA) processes

Parameter	Cd^{2+} (Cd^{2+} + MO) C_1 ($C_1 > C_2$)		Cd^{2+} (Cd^{2+} + MO) C_2 ($C_1 > C_2$)	
	Photo-Fenton	Fenton + Ads.	Photo-Fenton	Fenton + Ads
Adsorbent	FA + Fe^{2+} , H_2O_2	FA + Fe^{2+} , H_2O_2	FA + Fe^{2+} , H_2O_2	FA + Fe^{2+} , H_2O_2
q_e [mmol/g]	5.631	6.472	4.789	4.807
k_2 [g/mg · min]	1.575	2.838	0.002	0.009
R^2	0.978	0.973	1	1

Thus, by combining homogeneous photocatalysis and adsorption an improved process results, able to simultaneously remove multiple pollutants from wastewaters.

V. Novel Fly Ash - Based Adsorbents for Advanced Wastewater Treatment [140]

V.1. Novel Fly Ash - Based Substrates for Multi-Cation Wastewater Treatment

As previously mentioned, industrial wastewaters (e.g. from the electroplating industry) usually contain mixed pollutants and their removal runs, in adsorption, in concurrent processes.

Many compounds of heavy metals are easy soluble in water and can be adsorbed by living organisms part of the food chain. Some heavy metals (copper, cobalt, iron, manganese, vanadium, strontium and zinc) are accepted in small concentration for living organisms but excessive levels of essential metals can be detrimental to the organisms.

To minimize the human and environmental exposure to these hazardous heavy metals the US Environmental Protection Agency (US EPA) established the limits of Cadmium, Lead and Zinc that may be discharged into wastewater at: 0.01 mg/L, 0.006 mg/L, respectively 0.80 mg/L. The most common and widely used methods for advanced heavy metal removal are ion exchange, reverse osmosis, ultra filtration, electrochemical deposition and adsorption.

Although largely used in industry, adsorption, particularly ion exchange, presents several disadvantages like pH sensitivity, non-selectivity, and cost.

Heavy metals (cadmium, copper, zinc, nickel) removal was reported on scrap rubber, bituminous coal, peat, natural zeolite [238] while 4A zeolite synthesized by dehydroxylation of low grade kaolin is reported to remove Cu(II) and Zn(II) ions at neutral and alkaline pH.

The large majority of the studies report on mono- or bi-pollutant systems but industrial wastewaters have usually a more complex composition, thus occupying the adsorption sites depends on the components' affinity and substrate energy, and may lead to completely different efficiencies.

The investigations previously detailed proved that conditioning by alkali treatment (1N - 3N) can be a viable path for enhancing the adsorption efficiency of heavy metals [235] or multi-component systems of heavy metals and dyes [226]. This concentration is significantly lower compared with the 5-8 N usually reported.

For competitive, efficient multi-cation removal, the substrates need to have very good adsorption properties (specific surface, surface charge etc.) and controlled affinity. Additionally, the concurrent processes need to be investigated in multi-cation synthetic systems, used as simplified models for the advanced treatment of industrial (real) wastewaters.

Based on these assumptions a new set of experiments were done, including the aim of obtaining novel, zeolite-type substrates.

Class "F" fly ash (FA), collected from the Central Heat and Power (CHP) Plant Brasov (Romania), with oxides composition $\text{SiO}_2/\text{Al}_2\text{O}_3$ over 2.4 was used for obtaining a new substrate with good adsorption capacity for heavy metals from multi-cation wastewater treatment.

To activate fly ash, NaOH solution 3M was used at a 1/10 g/mL ratio between the sample and the activation solution. In the 1000 mL volumetric flask with reflux condenser, the new adsorbent was obtained from the slurry under stirring for 72 h, at atmospheric pressure and 100°C , on a thermo-stated heating plate. The new material was noted FA-Z and was comparatively analyzed with the washed fly ash (FA-W).

The diffractograms (Fig. 93) show that some crystalline phases of FA-W (quartz and mullite, cristobalite) are mostly absent in the new material (FA-Z), while the new crystalline phases in FA-Z are sodium aluminium silicate ($\text{Na}_6[\text{AlSiO}_4]_6 \cdot 4 \text{H}_2\text{O}$), sodium aluminium silicate hydrate (phillipsite), ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12 \text{H}_2\text{O}$), sodium aluminum silicate hydroxide hydrate, ($\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 4 \text{H}_2\text{O}$), clinoptilolite ($(\text{Na,K,Ca})_5(\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 18 \text{H}_2\text{O})$), tobermonite ($(\text{Ca,K,Na,H}_3\text{O})(\text{SiAl})\text{O}_3 \cdot \text{H}_2\text{O}$) and other phases of the aluminosilicates. This confirms that chemical restructuring occurs within FA-W. The crystalline degree of FA-Z is estimated at 45.65%.

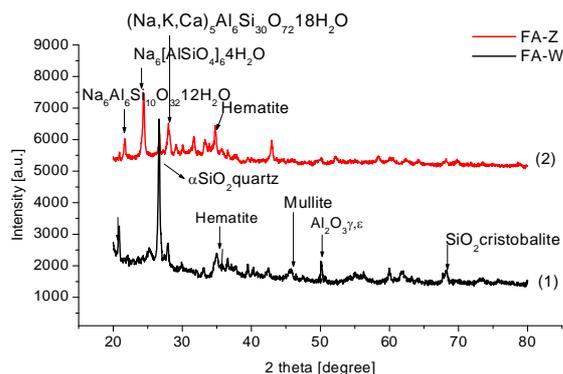


Fig. 93. XRD of (1) FA-W; (2) FA-Z [140]

Supplementary information was obtained using the FTIR spectra. The IR spectrum can be splitted on two groups of vibration: one is internal vibration of the framework units $(\text{SiO}_4)^-$ or $(\text{AlO}_4)^-$ and the other group of vibrations indicate the links between the framework units in the structure of FA-Z. The fly-ash based substrates have a composition close to a zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ over 2.4), therefore the frequency regions corresponding to different types of vibrations in zeolites, presented in Table 50 [263] were considered as reference in investigating the experimental results.

Table 50. Characteristics of IR bands associated with zeolite-A (common for all zeolites)

Type of IR band	Frequency [cm^{-1}]
Internal tetrahedral bonds	
Asymmetric stretch of $\text{T}^* - \text{O}$ bond	1500-950
Symmetric stretch of $\text{T}^* - \text{O}$ bond	660
External bonds	
Double ring	670-500
Symmetric stretch	750-820
Asymmetric stretch	1050-1150

*T = Si or Al

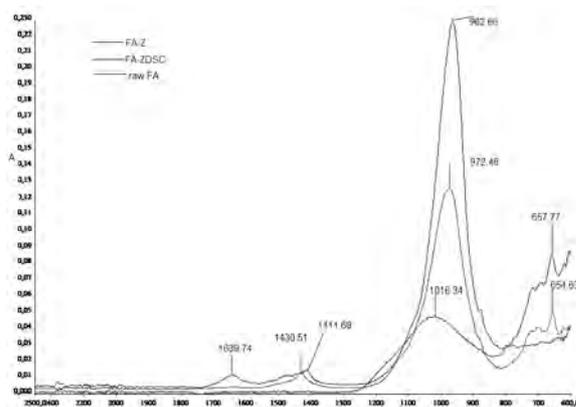


Fig. 94. IR spectrum (a) raw fly ash; (b) FA-Z; (c) FA-Z - DSC

By removing the soluble compounds there is a relaxation in the system, confirmed by the shift of the 950-1500 cm^{-1} absorbance band in the IR spectra of FA-W and FA-Z; this could be correlated with the substituted Al atoms in the tetrahedral forms of the silica frameworks. The IR spectrum of FA-Z shows a sharp peak with high intensity at 962.66 cm^{-1} , which can be assigned to the Si-Al-O asymmetric stretching while the band recorded at 657.77 cm^{-1} can be assigned to the Si-Al-O symmetric stretching. In this type of material, water molecules are associated with the cations and are in some extent hydrogen bonded to the oxygen ions of the framework, explaining the peak with less intensity, recorded at 1639.74 cm^{-1} which is characteristic of the bended mode in the water molecules.

To test the thermal stability and water bonding of the FA-Z material, DSC test were done (in nitrogen flow) with a scan rate: 2 $^{\circ}\text{C}/\text{min}$ at temperatures between 30-550 $^{\circ}\text{C}$. The IR spectrum of the sample after the DSC analysis is presented in Fig. 95b, confirming the water peak at 1639.74 cm^{-1} . The shift of the Si-Al-O asymmetric stretching peak to slightly higher values may also raise the possibility of the “lubricant” effect of the adsorbed water molecules within the FA-Z material.

The AFM images were used for surface morphology studies, Fig. 95.

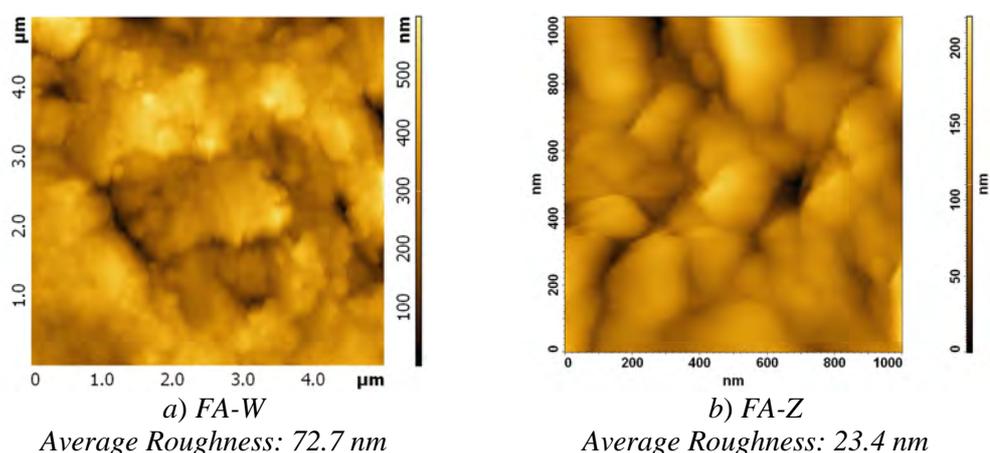


Fig. 95. AFM topography and average roughness [140]

The dissolution of the soluble compounds from raw FA lead to a new topography of the FA-W surface resulting in more homogeneous and smooth surfaces. But, the thermal alkali treatment for producing FA-Z is responsible for a significant reorganization at/of the surface as the AFM image in Fig. 95b confirms.

The surface area of the FA-W and FA-Z were analysed and the results show a strong increase in the specific surface, and a decrease in the average pores diameter; corroborated with the previous surface and structural data, these indicates a new type of organisation in the FA material.

The main characteristics of FA-W and type of zeolite FA-Z are presented in Table 51:

Table 51. *Characteristics of FA-W and FA-Z*

Sample	Specific surface area (BET) [m ² /g]	Micropores volume (t-plot) [cm ³ /g]	Micropores surface (t-plot) [m ² /g]	Average pores diameter [nm]
FA -W	6.14	0.0004	2.25	27.2
FA-Z	37.97	0.003	14.09	15.4

Cation adsorption involves mainly electrostatic forces therefore the surface energy of the new substrate (FA-Z) can strongly influence the adsorption process. The polar and dispersive contributions to the surface energy of FA-Z were calculated according to the model developed by Owens, Wendt, Robel and Kaelble and are presented in Table 52.

Table 52. *The energetic characteristic of FA-Z surface*

Surface Energy [mN/m]	Dispersive contribution [mN/m]	Polar contribution [mN/m]
207.52	32.61	174.91

The data show a high global surface energy and a large polar component, recommending the material as a good adsorption substrate.

The new adsorbent material obtained from CET fly ash was tested as adsorbent for simultaneous removal of Pb²⁺, Cd²⁺ and Zn²⁺ from three-cation solutions.

Two series of *adsorption experiment* tests were run on three-component solutions of Cd²⁺, 0...700 mg/L, Zn²⁺, 0...350 mg/L, respectively Pb²⁺, 0...1350 mg/L:

- The first set of experiments used the novel adsorbent (FA-Z)
- The second experimental series used commercial macroporous (Purolite C150, exchange capacity 1.8 Eq/L) and microporous cation exchangers (Purolite C100 gel, exchange capacity 2.0 Eq/L), selected as reference for the industrial solutions, now-a-days implemented.

To evaluate the adsorption efficiency and investigate the adsorption isotherms, the cations solutions were stirred up to 240 min at room temperature (20-25 °C), then the substrate was removed by vacuum filtration and the supernatant was analyzed.

The optimal contact time was evaluated on suspensions of 0.5 g FA-Z in 100 mL multicomponent solutions of Cd^{2+} (700 mg/L), Zn^{2+} (350 mg/L) respectively Pb^{2+} (1350 mg/L). Aliquots were taken each 15, ..., 240 min., when stirring was briefly interrupted and the substrate was removed by filtration. The residual metal concentrations in the supernatant were analyzed by AAS.

In all cases, the working pH value increased from 5.6 (natural pH value in the three - cations solutions with FA-Z) to 6.6 involving a slow release of the alkali traces resulted from synthesis.

Preliminary experiments proved that heavy metals losses due to adsorption to the container walls and to the filter paper were negligible.

The process parameters (contact time, substrate's dosage and initial cations' concentration) were optimized considering the maximum removal efficiency of Cd^{2+} , Pb^{2+} and Zn^{2+} ions, η , on FA-Z, was calculated.

The dynamic adsorption results are presented in Fig. 96a, b and c for the cadmium, lead and zinc adsorption on FA-Z.

The experimental data show a very efficient lead removal, after a very short contact time and on a broad concentration range.

The adsorption equilibrium for cadmium and zinc needs 90 min to be settled therefore, this was the set as optimal contact time in all further experiments. Also, for these two ions, higher substrate dosage is required, almost similar removal efficiencies (close to 70%) being registered at 1.3 g of FA-Z dispersed in 100 mL of solution, while a dosage of 0.5 g/100 mL allows almost complete lead removal.

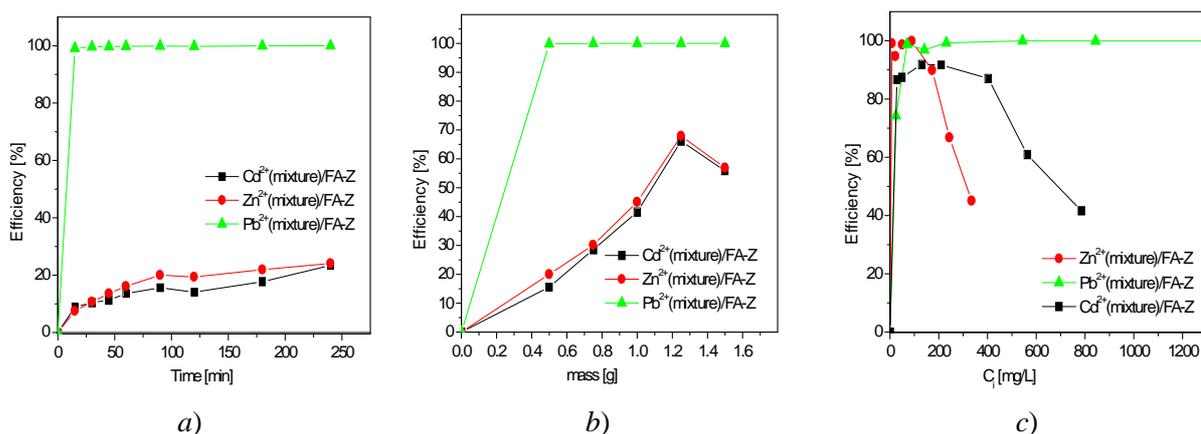


Fig. 96. a) Cd^{2+} , Pb^{2+} , Zn^{2+} ; Efficiency vs. contact time; $m_{ss} = 0.5$ g FA-Z/100 mL sol;
 b) Cd^{2+} , Pb^{2+} , Zn^{2+} ; Efficiency vs. m_{ss} of FA-Z/100 mL of sol; Contact time = 90 min;
 c) Cd^{2+} , Pb^{2+} , Zn^{2+} ; Efficiency vs. C_i [mg/L]; Contact time: 90 min; $m_{ss} = 0.75$ g

At high cation concentrations the adsorption efficiency is rather low for the large volume, hydrated cations (Cd^{2+} and Zn^{2+}). This observation can be explained by the ionic radii of the metal ions and also explains the data presented in Fig. 96a and 96b. If the hydrated shell is small, the removal efficiency increases, up to 99% for the Pb^{2+} cation, Table 53 [236].

Table 53. Properties of the dehydrated and hydrated heavy metal cations

Heavy metal	Cadmium	Lead	Zink
Anhydrous ionic radius [nm]	0.097	0.122	0.074
Hydrated ionic radius [nm]	0.426	0.261	0.430

These data can be linked with the cation's transport rate toward the substrate but can have also other reasons like occupying more active sites with a single large, hydrated cation or the need for supplementary reaction energy if adsorption occurs with dehydration. The data also show that cadmium and zinc have a much lower affinity for the FA-Z substrate, showing an efficiency decrease for contact times longer than 240 min, supporting the assumption of an adsorption process without dehydration.

The FA-Z substrate is highly efficient ($\eta > 90\%$) for the removal of all cations at concentrations below 100 ppm, thus for advanced wastewater treatment, another preliminary process is needed, e.g. pre-precipitation.

The adsorption studies carried out to estimate the heavy metal removal from wastewater, using fly ash, showed that the efficiency follows the order $Pb^{2+} > Zn^{2+} \geq Cd^{2+}$.

The adsorption efficiency of this new type of substrate was compared with those of C100 micro-porous and C150 macro-porous cation exchangers, in the same experimental conditions and the results are presented in Fig. 97.

As expected considering the participants in the processes, in all cases the adsorption efficiency on the microporous substrate is higher than on the macroporous. In lead removal, the FA-Z substrate is slightly more effective than the microporous ion exchanger. It is also to notice that for cadmium and zinc removal the macroporous cation exchanger gives almost similar results as FA-Z.

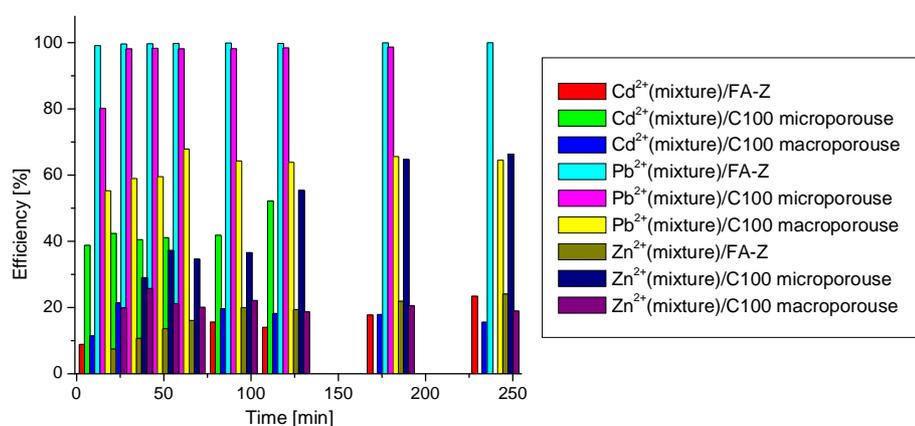


Fig. 97. Cd^{2+} , Pb^{2+} , Zn^{2+} , immobilization Efficiency vs. contact time [140]

The data recommend thus the FA-Z substrate for lead selective adsorption from complex cation mixtures, being also able to efficiently replace the cations exchanges in current lead removal processes even when mixed with other species.

The pseudo-second order kinetic model is based on the assumption that the rate limiting step may be a chemical adsorption involving the valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate [264]. The model is mentioned in literature for many systems, including Cu^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} adsorption on zeolites [265], Pb^{2+} and Cu^{2+} removal on humic acid [266], Cu^{2+} , Ni^{2+} , Cd^{2+} removal on fly ash from single- or double-pollutant solutions [225].

Another possible kinetic model which can be applied in adsorption processes on porous materials is the interparticle diffusion model. In this case, the amount of heavy metals ions adsorbed can be calculated with the Eq. (63):

$$q = k_{id} t^{1/2} + C . \quad (63)$$

These models were tested for the Cd^{2+} , Zn^{2+} and Pb^{2+} removal by adsorption on FA-Z and by ion exchange. The linearization proved that the pseudo-second order kinetic well describes the adsorption mechanism for all the three cations, on all the investigated substrates.

The results also proves that cadmium and zinc adsorption can follow more parallel mechanisms, which could be expected considering the FA-Z composition and/or the pores distribution with active sites of various energy. The kinetic parameters are presented in Table 54.

Table 54. Kinetic parameters of the heavy metal adsorption

Type of FA	n = 1		n = 2			Interparticle Diffusion		
	K_L [min^{-1}]	R^2	k_2 [$\text{g}/(\text{mg}\cdot\text{min})$]	q_e [mg/g]	R^2	K_{id} [$\text{mg}/\text{gmin}^{1/2}$]	C	R^2
Lead (Pb^{2+})								
FA-Z	-	0.833	$0.5 \cdot 10^{-4}$	2500	1	-	-	0.407
C100 microporous	-	0.366	$0.9 \cdot 10^{-4}$	2000	1	-	-	0.684
C150 macroporous	-	0.766	0.009	172.44	0.999	-	-	0.518
Cadmium (Cd^{2+})								
FA-Z	0.005	0.886	0.852	30.211	0.972	2.037	3.492	0.934
C100 microporous	-	0.231	0.133	79.365	0.969	-	-	0.662
C150 macroporous	0.017	0.881	0.286	37.453	0.995	-	-	0.740
Zinc (Zn^{2+})								
FA-Z	0.012	0.940	2.425	18.87	0.995	1.046	1.417	0.947
C100 microporous	2.929	0.918	1.355	59.171	0.913	2.929	1.757	0.954
C150 macroporous	-	0.011	0.002	12.854	0.995	-	-	0.318

As already outlined, lead speciation indicates the formation of $\text{Pb}_2(\text{OH})^{3+}$, $\text{Pb}_3(\text{OH})^{4+}$ or other poly-nuclear compounds in alkaline media but, in the working conditions ($\text{pH} < 7$) the lead cation is dehydrated/slightly hydrated. Considering the pseudo-second order kinetics, the lead adsorption rate is much lower comparing to the other two cations, supporting the conclusion that diffusion does not represent a limiting step in the processes on FA-Z or on cation exchangers. On the other hand, the Pb^{2+} adsorption capacity is high both on FA-Z (2500 $\text{mg-Pb}^{2+}/\text{g}$) and on C100 microporous (2000 $\text{mg Pb}^{2+}/\text{g}$) confirming that the FA-Z contains mezopores with a large number of active sites opened for the low volume lead cation.

The adsorption parameters were calculated considering the Langmuir and Freundlich Equations.

Table 55 presents the adsorption parameters for the heavy metal ions (Cd^{2+} , Zn^{2+} and Pb^{2+}) calculated from the slope of the linearization plots of the two isotherm equations.

Table 55. Adsorption parameters

Parameters	Langmuir Isotherm			Freundlich Isotherm		
	q_{\max} [mg/g]	a [L/mg]	R^2	n	K_F	R^2
FA-Z						
Cd/(Cd + Pb + Zn)	28.09	0.001	0.998	-	-	0.5
Pb/(Pb + Cd + Zn)	-	-	0.462	2.009	1354.94	0.992
Zn/(Zn + Cd + Pb)	13.38	0.002	0.999	-	-	0.356
C100 microporous						
Cd/(Cd + Pb + Zn)	59.17	0.001	0.999	-	-	0.708
Pb/(Pb + Cd + Zn)	144.93	0.001	0.999	1.933	54.66	0.911
Zn/(Zn + Cd + Pb)	30.86	0.001	0.999	1.618	14.01	0.961
C150 macroporous						
Cd/(Cd + Pb + Zn)	42.19	$2.37 \cdot 10^{-5}$	0.939	4.105	2.72	0.924
Pb/(Pb + Cd + Zn)	142.86	0.001	0.997	5.105	195.40	0.915
Zn/(Zn + Cd + Pb)	17.69	0.006	0.991	3.286	0.04	0.919

On the cation exchangers, chemisorption is the representative mechanism, as expected, for all the three cations, with the maximum adsorption capacity having values close to those obtained in the kinetic investigations, for the pseudo-second order mechanism, except lead adsorption on the microporous cation exchanger, where the values are significantly lower than those evaluated based on kinetic studies. Further adsorption-desorption studies will be employed to elucidate this aspect.

On FA-Z, the mono-layer adsorption described by the Langmuir equation supports the chemisorption mechanisms for the cadmium and zinc cations. The Cd^{2+} and Zn^{2+} cations can adsorb by chemically bonding with the active site ($\equiv\text{SiO}^-$) and ($\equiv\text{AlO}^-$) and can form complexes on the surface (Eq. 64, 65), as presented by [83]:



Lead ion adsorption could not be modelled by the Langmuir equation but, corroborating the data so far presented it is more likely that there are more chemisorption routes opened to lead (comparing to cadmium and zinc), as result of different active sites, with different energy, opened to this cation. The Freundlich equation, well describing lead adsorption, can support this type of approach.

The results indicate that the novel nano-substrate composite can be used as an efficient and low cost adsorbent for simultaneous removal of heavy metals from multi-cation solutions.

V.2. Novel Zeolite-Type Substrates Based on Fly Ash for Advanced Wastewater Treatment with a Complex Loaded [267]

The material described in the previous chapter showed that zeolite-type materials can be obtained starting from fly ash. One distinct feature of zeolite materials is their regular supra-structure, and this could be obtained by a control re-structuring of the fly ash oxide frames. One way to reach this ordering is by using templates, e.g. surfactants. The surface area and pore size of mesoporous silica materials can be tailored by different hydrothermal treatments [267] and the pore size was found to increase with the chain length of the surfactant, composition mixture, the pH value and temperature post synthesis [268, 269].

Thus a novel nano-substrate composite was developed; this is a mesoporous material obtained by hydrothermal method using alkali fly ash and Hexadecyltrimethylammonium bromide (98% purity, Sigma-Aldrich) (HTAB) $[\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3]\text{Br}^-$ at template. The amount of HTAB added was lower than the critical micelle concentrations ($\text{CMC}_{\text{HTAB}} = 298 \text{ mg/L}$), evaluated based on conductivity measurements.

Fly ash was washed (FAw), as previously described, then two materials were developed as follows:

- FAW was mixed with NaOH 2N solution and HTAB $[\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3]\text{Br}^-$, cationic surfactant in 1000 mL volumetric flask with reflux condenser further stirred (300 rpm) 24 hours at atmospheric pressure and 100°C , and was noted FAA-CS24.
- FAW was stirred in the same conditions for 48 hours and the sample was noted FAA-CS48.

The colloidal suspension was vacuum filtrated, washed repeatedly using ultra-pure water and dried at 115-125 °C till constant mass; the novel micro-nano material substrate was used in adsorption experiments of Cu^{2+} , Cd^{2+} cations from the bicomponent systems.

The XRD, Fig. 98 data show that the new substrates, FAA-CS24 and FAA-CS48, have well embedded the new phase of alumino-silicates. The crystallite sizes were calculated using the Scherrer Eq. (66) [269]:

$$\tau = \frac{K\lambda}{\beta \cos \theta}, \quad (66)$$

where: τ - is the size of crystallites; K - is the shape factor with a typical value 0.94; λ - is the X-ray wavelength (1.5406 Å); β - is the line broadening at half the maximum intensity (of a peak); θ - is diffraction angle.

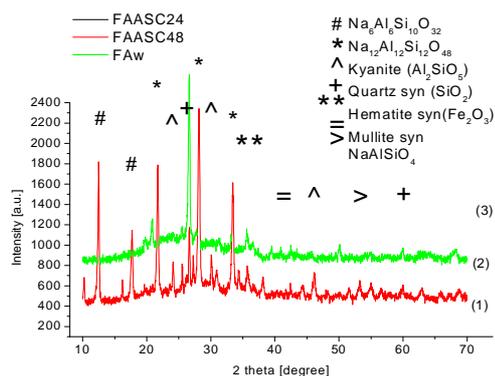


Fig. 98. XRD data of (1) FAW; (2) FAA-CS48 and (3) FAA-CS24 [267]

An increased crystalline is identified in the both substrates: quartz syn (with 135.9 Å crystallite size), sodium aluminium silicate ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}$ with 359.6 Å crystallite size), Kyanite (Al_2SiO_5 with 207.5 Å crystallite size) confirming that chemical restructuring occurs within FAW when hydro-thermally processed. The unburned carbon graphite, and carbon hexagonal (chaoite or white), along with compounds as micro-sized crystallites represents a significant part of the substrate and can explain the versatility of this material in adsorption processes of heavy metals, organic pollutants, including dyes [140]. The overall crystalline degree of FAA-CS is estimated at 66.66% the rest being represented by amorphous phases.

The crystalline modifications are accompanied by a significant increase in the BET surface, from 6.14 m^2/g in FAW at 62.57 m^2/g .

During long time washing under stirring in ultra-pure water, the soluble alkaline oxides, (K_2O , Na_2O , MgO , CaO) were removed from the raw fly ash surface into the solution, with a corresponding increase in the pH value (10.2), conductivity (1710 mS) and TDS, leading to grains with average roughness of 90.79 nm. The hydrothermal process of FAW and HTAB in the alkaline solution further promotes surface interactions, including dissolution, recrystallization of the FAW components and new aluminosilicates had developed by reaction of $NaOH$ with silica from quartz. The result is a much rougher surface (123.6 nm). Increasing the value roughness signifies increasing defects in the surface and a possible increase in the number of high energy active site, Fig. 99b.

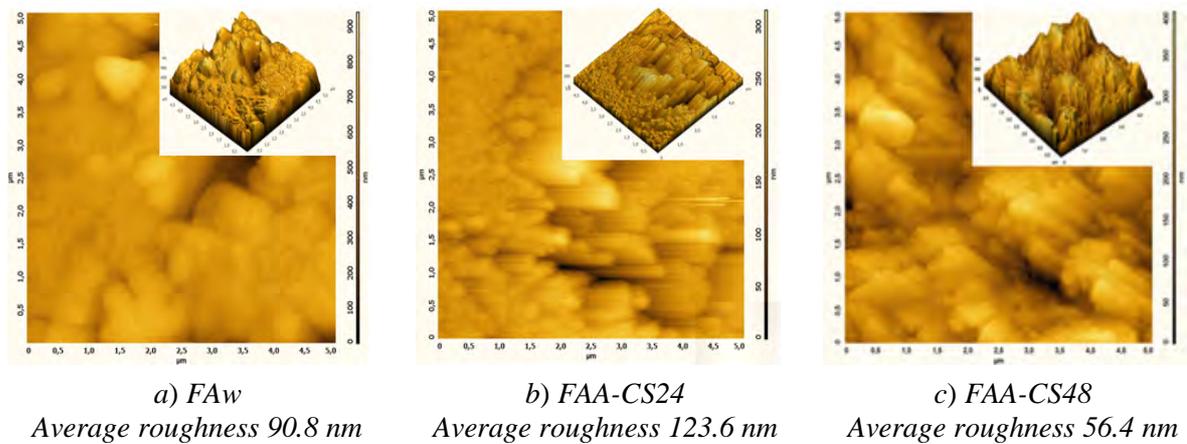


Fig. 99. AFM images for: a) FAW; b) FAA-CS24; c) FAA-CS48 [267]

As the images in Fig. 100 show, the FAA-CS grains are significantly larger (3.37...90.5 μm) than the individual particles, or agglomerations developed on spherical grains of fly ash particles.

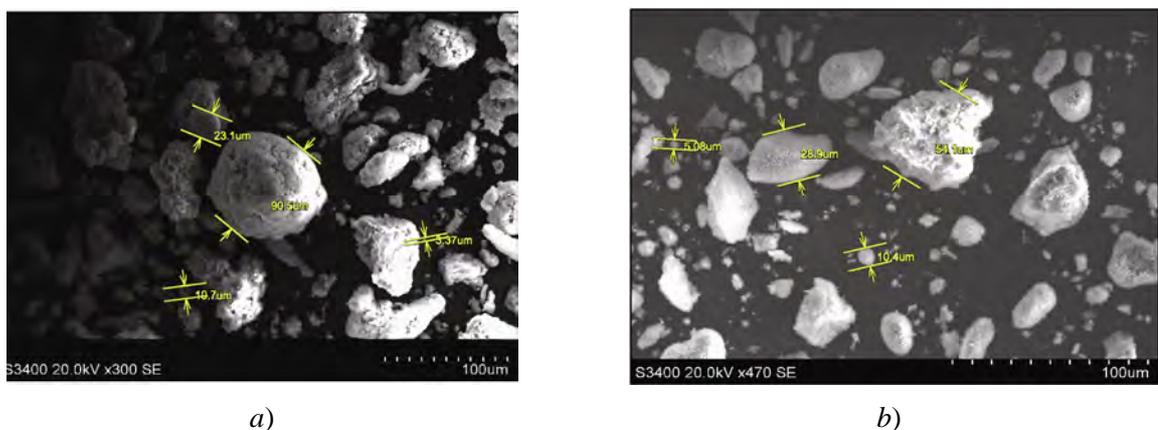


Fig. 100. SEM images of: a) FAA-CS24 and of b) FAA-CS48

The elemental EDS analysis of FAA-CS24 is shown in Fig. 101.

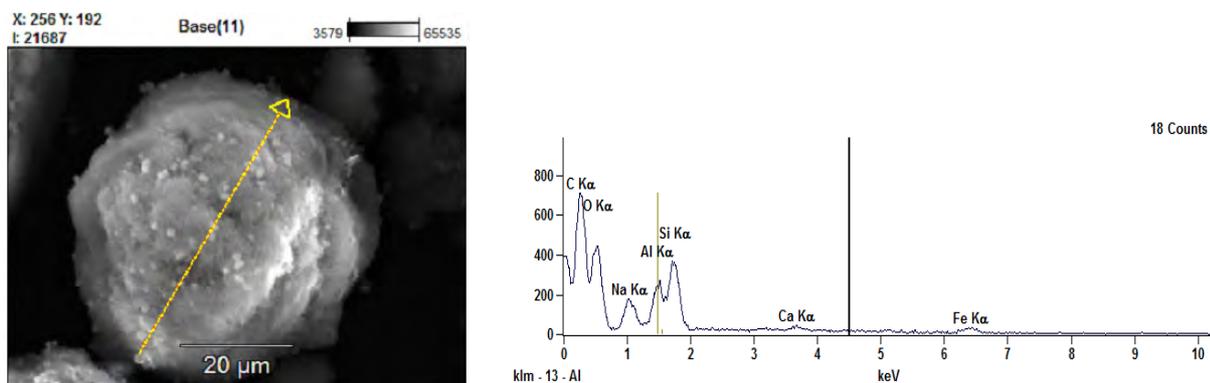


Fig. 101. EDS spectra of FAA-CS24 before adsorption

The elemental EDS analysis of FAA-CS24 and FAA-CS48 samples show high intensity signals for Si, Al, Na, O, and confirm the Cd, N and S atoms on the surface of substrate scanned after adsorption Table 56.

Table 56. Surface composition, in atomic %, of the FAA-CS48 surface before and after adsorption the (Cd^{2+} + MB) solution

Element	FAA-CS24		FAA-CS48	
	Before adsorption	After adsorption	Before adsorption	After adsorption
N	16.40	-	-	9.09
O	39.50	-	39.48	72.23
Na	2.53	1.58	4.64	1.71
K		1.22		-
Al	3.16	10.08	3.23	5.56
Si	5.45	28.53	8.93	8.93
S	-	1.92	-	0.19
Ca	1.67	-	0.19	0.17
Ti	0.12	1.49	0.17	0.16
Br	-	7.68	-	0.00
Cd	-	27.00	-	1.96

This results show that the fly ash has potential to be used as an alternative and cheap source of silica or alumino-silicates in the production of adsorbents.

Micro-nano substrate was obtained in a hydrothermal process, starting from fly ash powder and HTAB cationic surfactant and was tested for simultaneous removal of heavy metal cations and dyes, in a single step process by adsorption.

The FAA-CS24 structural, morphology analysis and pore distribution showed that the substrate has a high crystallinity degree and a surface with broad open pores, efficient in heavy metals (Cd^{2+} and/or Cu^{2+}) removal from systems also containing Methylene Blue.

The SEM and AFM images, Fig. 102a and b, show modified surfaces due to adsorption processes of the MB and the Cd^{2+} , Cu^{2+} ions, confirmed by roughness modification.

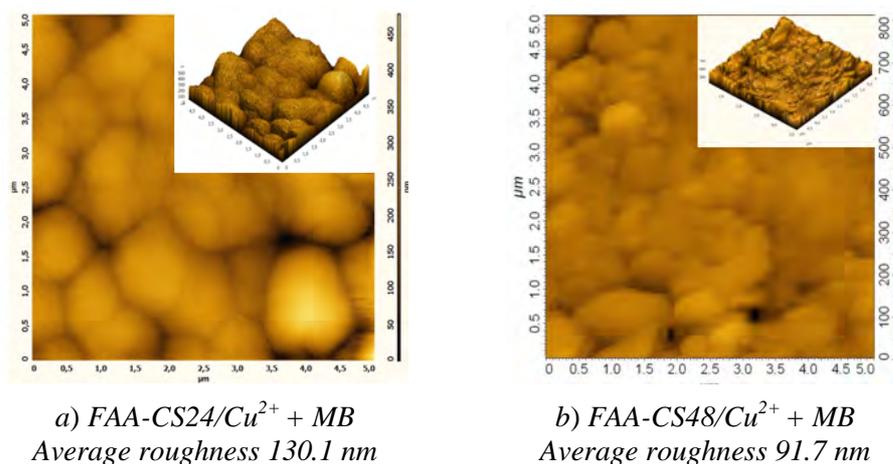


Fig. 102. AFM images after adsorption process

These AFM images were used to characterize the surface morphology: the uniformity, grain size and pore size distribution of the samples Fig. 103.

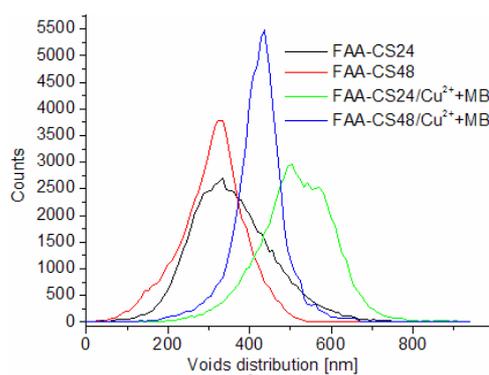


Fig. 103. The interparticle voids distribution

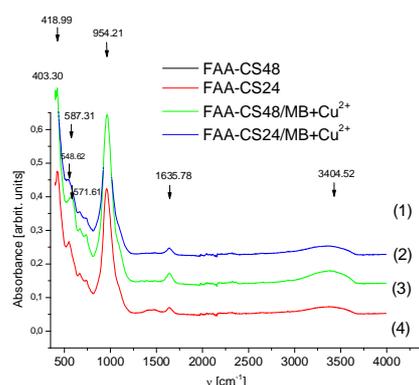
Supplementary information was obtained using the FTIR spectra. The fly-ash based substrate has a composition close to a zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ over 2.4), therefore the frequency regions corresponding to different types of vibrations in zeolites, presented in Table 57 were considered as reference [263] in investigating the experimental results.

Table 57. Characteristics of IR bands associated with zeolites (common for all zeolites)

Type of IR band vibrational	Frequency [cm ⁻¹]
<i>Internal tetrahedral</i>	
Pore opening vibrations	300-420
T-O bending vibration	420-500
Symmetric stretch of T-O bond	660
<i>External tetrahedral</i>	
Double ring vibration	500-670
Symmetric stretch	750-820
Asymmetric stretch of T-O bond	950-1500
Asymmetric stretch	1050-1150

T = Si or Al.

Fig. 104 illustrates the FTIR spectra of the substrates before and after adsorption. The asymmetric stretching modes of Si-O-Si or Si-Al-O in all samples analysis was suggested by the absorption band at 954.21 cm⁻¹ for all with sharp peak, indicating the links between the framework units in the structure of FAA-CS. The absorption band observed from 3200-3600 cm⁻¹ was attributed the hydroxyl group stretching/vibration in Si-OH, Al-OH-Al, Si-OH-Al units. IR spectroscopic studies conducted by Rayalu et al. [271] showed that there was good agreement between IR and the XRD analysis.

**Fig. 104.** IR spectrum: (1) FAA-CS48; (2) FAA-CS24; (3) FAA-CS48/MB + Cu²⁺; (4) FAA-CS24/MB + Cu²⁺ after adsorption

The kinetic and thermodynamic studies show that the substrate has a good adsorption capacity mainly based on the electrostatic attractions between the substrate and Cd²⁺, Cu²⁺ and their mixed solutions.

Based on the Pourbaix diagrams [272] it may be concluded that cadmium cations are not significantly hydrolysed in the working conditions (pH_{Cd, hydrolysis} > 9) while the copper ion could be found as Cu(OH)⁺, at pH values above 6.8.

The experimental conditions were:

- FAA-CS24: working pH = 8.22, $pH_{PZC1 \text{ FAA-CS24}} = 7.80$ and $pH_{PZC2 \text{ FAA-CS24}} = 5.72$;
- FAA-CS48: working pH = 9.56, $pH_{PZC1 \text{ FAA-CS48}} = 8.34$ and $pH_{PZC2 \text{ FAA-CS48}} = 5.27$.

In these conditions, the FA matrix preserves an overall negative surface charge supporting the adsorption of the cationic species (heavy metals and S^+ from MB) in concurrent processes based on electrostatic attractive forces and influenced by the volume of the species.

The adsorption efficiency, η , was evaluated with Eq. (67):

$$\eta = \frac{(c_{HM/MB}^i - c_{HM/MB}^e) \times 100}{c_{HM/MB}^i} \quad (67)$$

Good removal efficiencies are obtained after 120 min. for heavy metals and for MB, Fig. 105a and Fig. 105b. Increased efficiencies over 90% for MB, 60% for cadmium and 71% for copper in adsorption processes are mainly related to the mechanical stirring employed in this set of experiments. The data from Fig. 105a, b, indicate a similar removal mechanism both for the hydrated copper cations and MB.

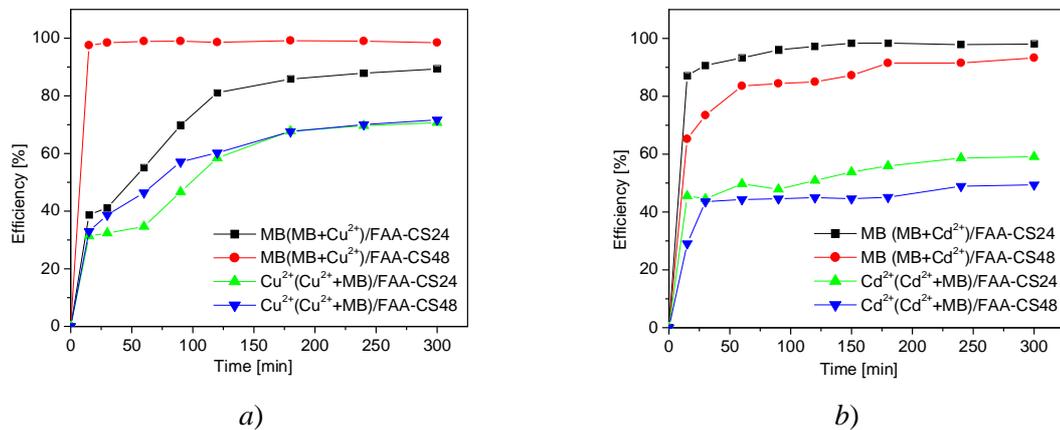


Fig. 105. The influence of type of substrate in removing the Cd^{2+} , Cu^{2+} and MB from pollutant system by adsorption processes

These data correlated with the elemental EDS analysis of substrates Table 56 indicate that both substrates are effective in removing the pollutants by adsorption process but, one of the two substrates, FAA-CS24 is more economically feasible as the processing time is shorter thus the energy consumption is lower. Therefore, further investigations used this substrate.

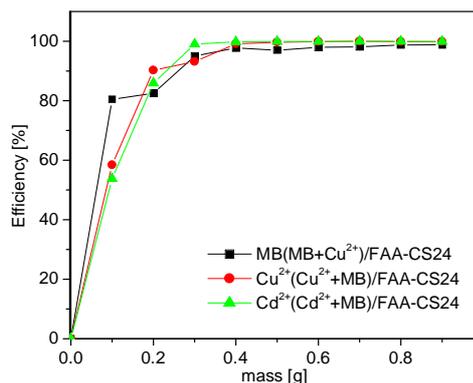


Fig. 106. Removal efficiency of HM cations and MB vs. FAA-CS24 substrate dose in adsorption process

The removal efficiency of heavy metals from solution with two pollutants (HM cations and MB) is much higher for all pollutants (Cu^{2+} , Cd^{2+} cations and MB) Fig. 106, as result of the increase of the substrate dosage implicit of the active sites.

In all cases after a rapid adsorption of cadmium, copper cations and methylene blue (Fig. 105), adsorption slowly reached equilibrium at 120 min.

Using the linear form of the kinetics models, the kinetic parameters are presented in Table 58 and show that all three mechanisms can run (particularly on FAA-CS24), as result of a substrate with increased heterogeneity, coming from its intrinsic nature and from various compositions of the monolayers that can be formed during the complex processes of adsorption.

Table 58. Kinetic parameters of the heavy metal adsorption

Substrate	Pseudo first-order kinetics		Pseudo-second order kinetics			Interparticle Diffusion		
	K_L [min^{-1}]	R^2	k_2 [$\text{g}/\text{mg}\cdot\text{min}$]	q_e [mg/g]	R^2	K_{id} [$\text{mg}/\text{g}\cdot\text{min}^{1/2}$]	C	R^2
$\text{Cu}^{2+}(\text{Cu}^{2+} + \text{MB})$								
FAA-CS24	0.005	0.953	0.446	119.058	0.969	5.754	11.554	0.939
FAA-CS48	0.014	0.992	0.231	138.889	0.996	5.330	42.240	0.951
$\text{Cd}^{2+}(\text{Cd}^{2+} + \text{MB})$								
FAA-CS24	0.013	0.888	0.097	156.25	0.995	2.989	101.0	0.929
FAA-CS48	-	0.696	0.055	126.582	0.993	-	-	0.613
$\text{MB}(\text{MB} + \text{Cu}^{2+})$								
FAA-CS24	0.017	0.987	21.754	1.707	0.994	0.0861	0.227	0.916
FAA-CS48	-	0.312	0.089	1.649	1	-	-	0.314
$\text{MB}(\text{MB} + \text{Cd}^{2+})$								
FAA-CS24	0.048	0.870	1.134	1.613	0.999	0.016	1.394	0.873
FAA-CS48	-	0.728	6.225	1.634	0.999	0.365	1.056	0.880

V.3. Novel Fly Ash TiO₂ Composites for Simultaneous Removal of Heavy Metals and Surfactants [129]

A novel, cost-effective substrate is obtained by hydrothermal processing from fly ash (CPH- Brasov, Romania) coated with a wide band gap semiconductor, TiO₂. The new substrate is used for removing, in a single step process, heavy metals (Cd²⁺, and Cu²⁺) and surfactants: 1-Hexadecyltrimethylammonium bromide - HTAB (CS) and dodecylbenzenesulfonate - SDBS (AS) from synthetic wastewaters containing two (one heavy metal + one surfactant) and three pollutants (two heavy metals + one surfactant).

Among the mostly used surfactants is hexadecyltrimethylammonium bromide (HTAB), a cationic surfactant being also effective as antiseptic agent against bacteria and fungi, and sodium dodecylbenzenesulfonate (SDBS), used in detergents composition, representing about half of the surfactants used now days.

Surfactants can produce foams, which represent a problem in sewage treatment; therefore biological processes based on activated sludge are problematic and, alternatively, surfactants adsorption was intensively studied on various adsorbents, such as activated carbon, rubber granules, layered double hydroxides, silica, mineral oxides and natural biomasses, leather waste. Photocatalysis is also reported as efficient.

Following the concepts already formulated and tested, a novel mixed adsorbent - photocatalyst substrate was prepared using TiO₂ - Degussa and FAW in a 5:1 weight ratio, in NaOH 2N alkaline solution; in the 1000 mL volumetric flask with reflux condenser, the new adsorbent (FA-TiO₂) was obtained from the slurry under stirring (300 rpm) for 24 h, at atmospheric pressure and 100 °C, on a thermostet heating plate. After filtration, washing and drying at 105-120 °C was sieved and the 20-40 µm fraction was selected for adsorption experiments.

The pollutant systems were synthetically prepared using bidistilled water and CdCl₂ · 2.5 H₂O, CuCl₂ · 2 H₂O, SDBS (CH₃(CH₂)₁₁C₆H₄SO₃Na) and HTAB ([CH₃(CH₂)₁₅N⁺(CH₃)₃]Br⁻). The initial concentrations were: c_{HTAB} = 100 mg/L and c_{SDBS} = 150 mg/L, being lower than the critical micelle concentrations (CMC_{HTAB} = 298 mg/L and CMC_{SDBS} = 418 mg/L), evaluated based on conductivity measurements.

The solutions were used at their natural pH; the initial pH of the solutions containing surfactants and heavy metals in contact with FA-TiO₂ was 6.53, which is higher than the TiO₂ point of zero charge (PZC = 6.25), allowing thus a slightly negative charge on the photocatalyst.

Four series of experimental tests of adsorption and photocatalysis were done:

(a) in solutions containing two pollutants:

- Adsorption: Cd²⁺ and AS, under mechanical stirring;
- Adsorption: Cd²⁺ and CS, under mechanical stirring;
- Photocatalysis: Cd²⁺ and AS, under UV irradiation;
- Photocatalysis: Cd²⁺ and CS, under UV irradiation;

(b) in solutions containing three pollutant:

- Adsorption: Cd²⁺, Cu²⁺ and AS, under mechanical stirring;
- Adsorption: Cd²⁺, Cu²⁺ and CS, under mechanical stirring;
- Photocatalysis: Cd²⁺, Cu²⁺ and AS, under UV irradiation;
- Photocatalysis: Cd²⁺, Cu²⁺ and CS, under UV irradiation;

The thermodynamic and kinetic adsorption parameters of the heavy metals and surfactants from bi- and three pollutant systems were evaluated from batch experiments; in each experiment, 0.25 g of FA-TiO₂ substrate was stirred (200 rpm) at room temperature (20-23 °C), with 50 mL solutions, at initial concentrations set according to the experimental study; in the kinetic studies, aliquots were taken each at 15, ..., 240 min., when stirring was briefly interrupted and the substrate was removed by centrifugation.

The supernatant was further analyzed by AAS and UV-VIS absorbance measurements were done at the maximum absorption wavelength (224 nm) for SDBS. The concentration of HTAB in the supernatant was calculated from the concentration - surface tension curve, obtained based on the sessile drop method (Contact Angle System CA20).

The XRD data show that the new substrate, FA-TiO₂, has well embedded the anatase phase (anatase syn with 281.6Å crystallite size), while the characteristic (110) and (101) peaks of rutile were not identified, proving polymorph modifications even at the rather low processing temperature. The crystallite sizes were calculated using the Scherrer Eq.

The overall crystalline degree of FA-TiO₂ is estimated at 82.53% the rest being represented by amorphous phases.

The crystalline modifications are accompanied by a significant increase in the BET surface, from 6.14 m²/g in FAW to 37.97 m²/g in FA-TiO₂.

The hydrothermal process of FAW and TiO₂ further promotes surface interactions, including dissolution, re-crystallization of the FAW components and new components development, TiO₂ adsorption etc. The result is a much rougher surface (244 nm), Fig. 107, suitable for adsorption as result of a large amount of high energy active sites.

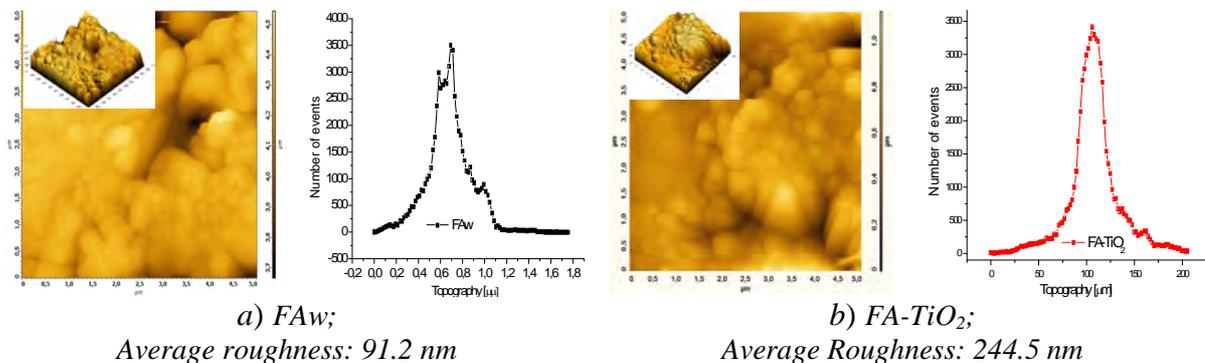


Fig. 107. AFM images and pores histograms for: a) FAW and b) FA-TiO₂

The adsorption processes are confirmed by the XRD data of FA-TiO₂ registered before and after adsorption of (Cd²⁺ + SDBS), Fig. 108, which show new peaks, corresponding to Na₂S₂O₇ and CdSO₃, indicating a possible formation of chemical bonds between the adsorbed species and the activated sites of the substrate.

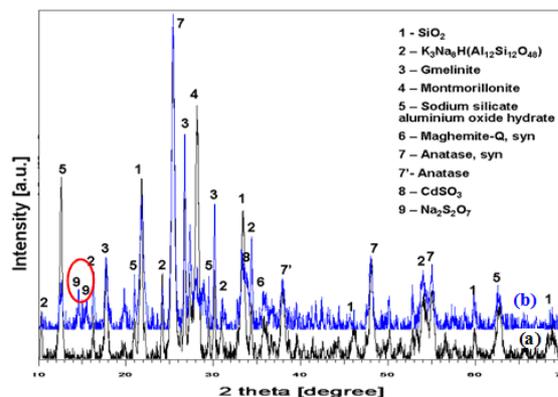


Fig. 108. XRD of FA-TiO₂ (a) before and (b) after contact with the (Cd²⁺ + SDBS) solution

Based on the high content of functional groups as $(\text{SiO}_4)^-$, $(\text{AlO}_4)^-$ or Ti-O-Si, the FA-TiO₂ substrate could develop electrostatic bonds with the hydrophilic parts of the surfactants. The elemental EDS analysis of FA-TiO₂ sample shows high intensity signals for Si, Ti, Al, Na, O, Fig. 109a, and confirm the Cd and S atoms on the substrate after adsorption Fig. 109b and Table 57. The data also show that during adsorption some cations (Na^+ , K^+ , Ca^{2+}) are totally or partially removed from the surface as possible result of dissolution; since the substrate was washed after preparation, one may consider that this is the result of surfactant interaction with the adsorption system.

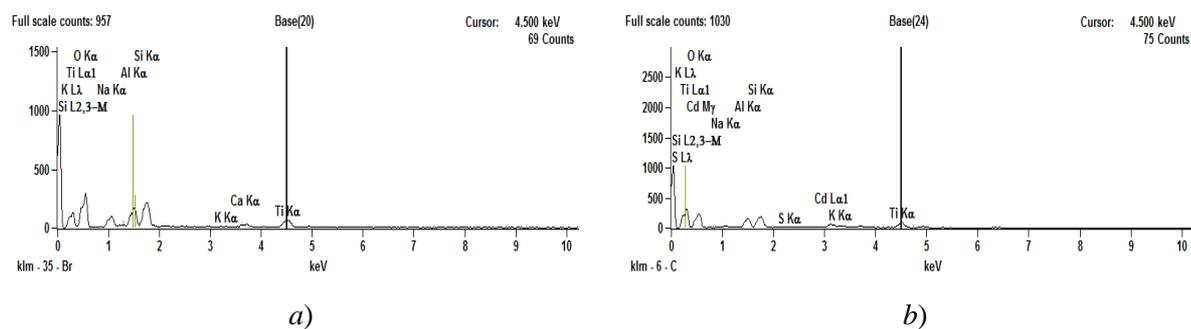


Fig. 109. EDS spectra of FA-TiO₂ (a) before and (b) after contact with the (Cd^{2+} + SDBS)

The Ti distribution along FA grains was analysed by SEM-EDS by measuring the atomic concentration at 20.0 kV. The Ti distribution is relatively homogeneous among Ti/Si and Ti/Al, proving an undifferentiated affinity of the FA major components for titanium.

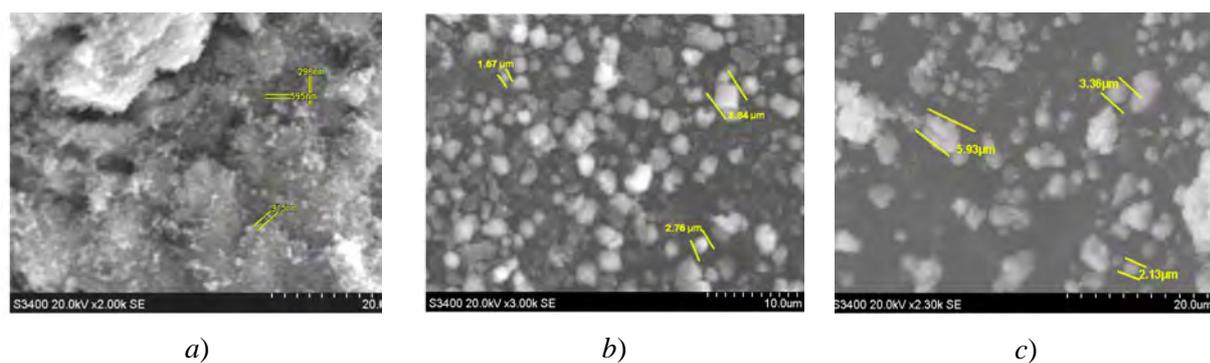
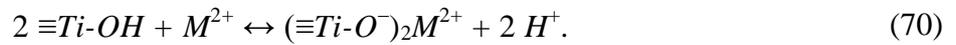


Fig. 110. SEM image of (a) Degussa P25, and of the FA-TiO₂ substrate (b) before and (c) after contact with the (Cd^{2+} + SDBS) solution

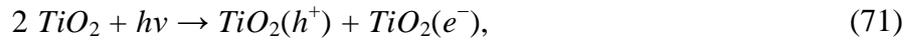
As the images in Fig. 110 show, the FA-TiO₂ grains are significantly larger (3...9 μm) than the TiO₂ P25 individual particles, supporting their technological recovery in a continuous wastewater treatment process. During the contact with the (Cd^{2+} + SDBS) solution agglomerations are developed; the cubic and spherical crystals in Fig. 110c are typical titanium dioxide, which can promote the larger cluster formation (up to 6 μm size) on the fly ash particles.

The substrates were tested in adsorption and photocatalysis. For both cations, the anionic combinations require pH values above 10 and are not likely to be formed in the working conditions.

According to the “site binding” theory, the surface charge on the metal oxides is created by the electrolyte ions adsorption, in protolytic equilibria. These processes for TiO₂ can be described by the following Eqs. [253]:



The photocatalytic processes on TiO₂ involves the formation of active oxidant species as HO•, when the photocatalyst is irradiated with energy higher than the band gap value (E_g = 3.1 eV, corresponding to a radiation with a wavelength of 399.9 nm):



The photocatalytic mechanism is effective when the pollutant is adsorbed or in the near vicinity of the catalyst surface, therefore, similarly to adsorption, the surface charge is important.

Considering the experimental conditions (working pH = 6.53, p*H*_{PZC, Degussa} = 6.25) on the FA-TiO₂ substrate the titanium dioxide component will be slightly negatively charged, while the FA matrix preserves an overall negative surface charge. Under these conditions, cationic species (HTAB, heavy metals, Na⁺ from SDBS) are supposed to be adsorbed, in concurrent processes based on electrostatic attractive forces, while the adsorption of the anionic surfactant SDBS would be less favored. At the same time, the positive charges on the TiO₂ surface may support an increased amount of HO•.

Good removal efficiencies are obtained in all cases after 120 min, Fig. 111, and further thermodynamic studies used this optimized contact time. Increased efficiencies in adsorption

processes (denoted with A) are mainly related to the mechanical stirring employed in this set of experiments, while photocatalysis experiments (denoted with F) were done without stirring, still reaching high efficiencies (close to 80%). In both processes, HTAB addition resulted in lower cadmium adsorption efficiencies, indicating a competitive process of both cations.

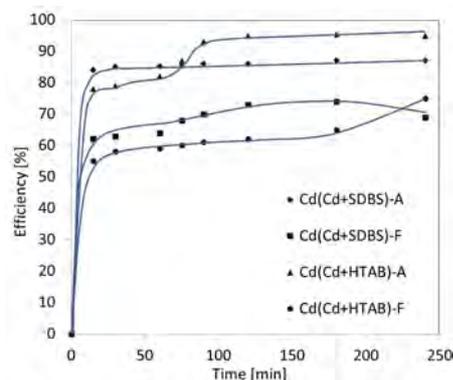


Fig. 111. Removal efficiency vs. time for: Cd^{2+} from the solution also containing surfactants, in adsorption (A) and photodegradation (F) processes

On the other hand, as expected, the SDBS removal is more efficient in photocatalytic than in adsorption processes, although higher efficiency values are registered after 240 min, which is in good agreement with previous results, obtained for dyes removal, when the optimal duration was also found to be 240 min [129]. For the technological optimal contact time (120 min), SDBS removal runs with 24% efficiency and doubling the contact time brings less than 10% increase, raising cost operating problems.

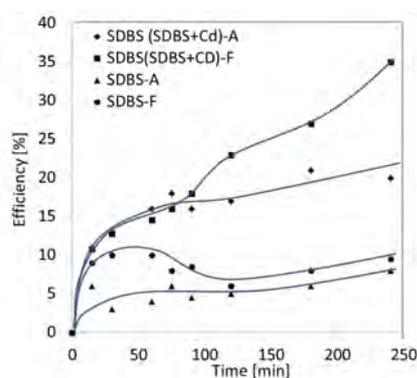


Fig. 112. Removal efficiency vs. time of SDBS from single pollutant solutions and from solutions also containing Cd^{2+} , in adsorption (A) and photodegradation (F) processes

An activation effect is registered in solutions also containing cadmium, both in adsorption and in photocatalysis Fig. 112. Further investigations will have to clarify if this is a result of a fast Cd^{2+} adsorption, developing potential higher active sites and/or if chemical interaction SDBS-Cd occurs on the substrate (as indicated by the XRD results, in Fig. 108). So far, the results

prove that there is no obvious competition between SDBS and Cd^{2+} removal, supporting the assumption that all these processes are primarily governed by electrostatic interactions.

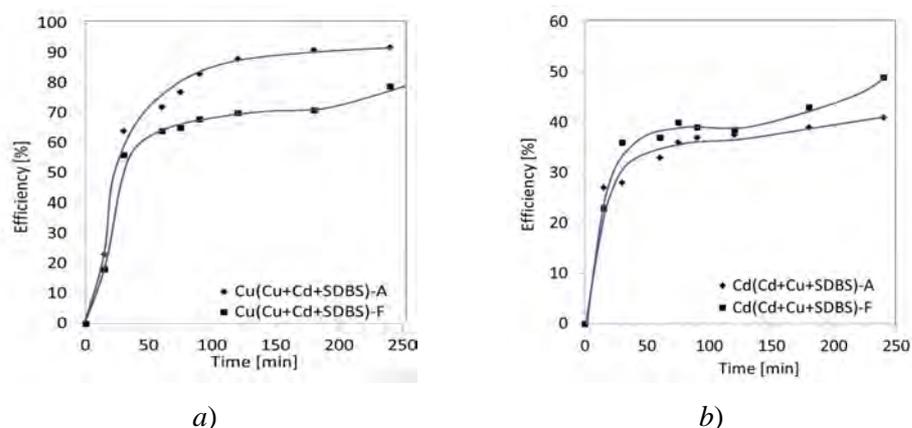


Fig. 113. Removal efficiency vs. time of Cu^{2+} (a) and Cd^{2+} from solutions also containing SDBS (b)

The removal efficiency of heavy metals from solution with three pollutants (Cd^{2+} , Cu^{2+} and SDBS) is much higher for the copper cations, Fig. 113, both in adsorption and photocatalysis, as result of the higher mobility of the Cu^{2+} (tetrahydrated) as compared with the hexahydrated Cd^{2+} , with larger volume.

Increased efficiency during photocatalysis can also be the result of copper-complexes formation with the by-products resulted in SDBS oxidation, with higher affinity for the substrate.

The amount of FA- TiO_2 in the removal processes was optimised considering the highest risk pollutants, the cadmium cation and HTAB, was set at 0.4 g FA- TiO_2 in 50 mL pollutant solution.

The mechanism of adsorption was modelled with pseudo-first order kinetic and interparticle diffusion, models which can be applied in the adsorption on highly porous materials.

The kinetic parameters are listed in Table 59.

Table 59. Kinetic parameters of the heavy metal adsorption

Investigated cation (System)	Process	Pseudo-second order kinetics			Interparticle Diffusion		
		k_2 [g/mg·min]	q_e [mg/g]	R^2	K_{id} [mg/gmin ^{1/2}]	C	R^2
Cd ²⁺ (Cd ²⁺ + AS)	UV irradiation	0.038	103.1	0.996	2.464	72.72	0.959
Cd ²⁺ (Cd ²⁺ + AS)	Adsorption	0.014	125.0	0.999	-	-	0.746
Cd ²⁺ (Cd ²⁺ + Cu ²⁺ + AS)	UV irradiation	0.331	69.4	0.991	1.635	37.55	0.921
Cd ²⁺ (Cd ²⁺ + Cu ²⁺ + AS)	Adsorption	0.271	59.2	0.998	1.318	36.30	0.91
Cu ²⁺ (Cu ²⁺ + Cd ²⁺ + AS)	UV irradiation	0.556	55.9	0.978	3.142	8.43	0.806
Cu ²⁺ (Cu ²⁺ + Cd ²⁺ + AS)	Adsorption	0.471	64.1	0.978	4.401	5.40	0.867
Cd ²⁺ (Cd ²⁺ + CS)	UV irradiation	0.110	95.2	0.992	2.278	58.46	0.968
Cd ²⁺ (Cd ²⁺ + CS)	Adsorption	0.079	123.4	0.998	2.491	83.34	0.934
Cd ²⁺ (Cd ²⁺ + Cu ²⁺ + CS)	Adsorption	0.283	14.5	0.990	-	-	0.739
Cu ²⁺ (Cu ²⁺ + Cd ²⁺ + CS)	Adsorption	0.767	24.3	0.997	0.837	0.93	0.929

The rate constants are high, especially under UV irradiation confirming that there is a competition between cations and surfactants for occupying the active sites. During UV irradiation, surfactants are photo-degraded, being removed from the FA-TiO₂ substrate, leaving more active sites for cation adsorption. The data also show that during irradiation parallel mechanisms (pseudo-second order kinetic and interparticle diffusion) are likely, confirming once again that surfactant adsorption can be fast and, in adsorption processes can partially block the active sites.

Considering the adsorption processes, the data indicate that the large volume of HTAB allows the rapid adsorption of the cations, leading to higher rate constants, as compared to SDBS.

Copper adsorption is faster, as already indicated by the increased efficiencies; the fastest process corresponds to systems containing HTAB

The adsorption isotherm data were experimentally obtained based on the optimised contact duration (120 min) and substrate amount (0.4 g FA-TiO₂ in 50 mL solution). The adsorption parameters were calculated considering the Langmuir and Freundlich equations.

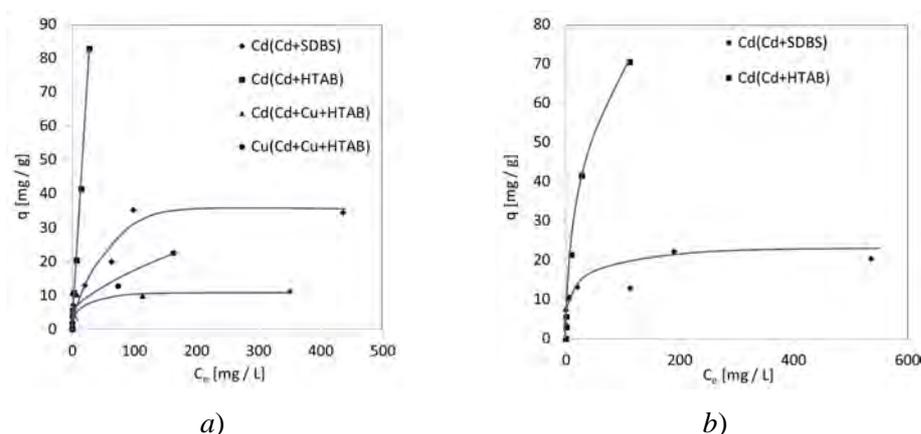


Fig. 114. Adsorption isotherms on the FA-TiO₂ substrate without (a) and with (b) UV irradiation

Table 60. Adsorption parameters

Cation (System) Conditions	Langmuir Isotherm			Freundlich Isotherm		
	q_{\max} [mg/g]	a [L/mg]	R^2	n	K_F	R^2
Cd ²⁺ (Cd ²⁺ + CS) UV irradiation	80.6	0.003	0.958	1.863	0.085	0.983
Cd ²⁺ (Cd ²⁺ + CS) Adsorption	86.2	0.003	0.942	1.934	0.142	0.959
Cd ²⁺ (Cd ²⁺ + AS) UV irradiation	21.0	0.046	0.965	1.838	0.351	0.884
Cd ²⁺ (Cd ²⁺ + AS) Adsorption	35.8	0.014	0.985	3.972	0.309	0.948
Cd ²⁺ (Cd ²⁺ + Cu ²⁺ + CS) Adsorption	13.9	0.075	0.987	1.863	0.085	0.983
Cu ²⁺ (Cu ²⁺ + Cd ²⁺ + CS) Adsorption	21.0	0.015	0.914	4.023	0.072	0.896

VI. Conclusions on the Original Research

Fly ash (FA) represents a waste which raises huge environmental concerns. Although industrial reuse is already implemented, the fly ash amounts are much larger; therefore novel recycling solutions are continuously searched, for advanced reuse, increasing the added value. Currently about 50% of the fly ash is used for construction materials but still the burden imposed on environment is high. Therefore, novel applications of fly ash are required.

One way to use fly ash is in developing novel and efficient solutions for advanced wastewater treatment. To increase its efficiency and reproducibility a novel concept was proposed in the research plan, by developing substrates able to simultaneously remove inorganic and organic pollutants in a “one step” process”.

The results presented in this work represent a concise synthesis on the research activity on the new adsorbents materials that - besides efficiency, also meet several targets: they are low cost, they can be developed in accessible, up-scalable processes and they can be used in the removal of a wide range of pollutants: heavy metals, dyes, surfactants.

The main conclusions of the study are:

1. The fly ash substrate needs a pre-treatment (conditioning) before use

- The composition of fly ashes depends of the type of coal burned by the type of coal-fired boiler furnace and coal combustion technology. According to the ASTM C618 standard and the chemical composition, most fly ashes are of class F (the total percentage of SiO_2 , Al_2O_3 , Fe_2O_3 is over 75%), thus it will not aggregate in water. The microelements Ba, Cu, Zr, Sn, Pb, As, Ni, Zn, Ti, Cr, V can exist in fly ashes in the ppm order.
- Raw fly ash contains soluble compounds that must be removed by long term washing (48 h), thus a conditioning step (involving long term contact with water) is necessary before the use of the second raw material as collected.

- The raw fly ash has a highly heterogeneous surface composition and charge which makes it unsuitable for adsorption processes design. Further conditioning would thus be necessary when using fly ash.
- The choice of the chemical reagent is important and must target: (i) the increase in the specific surface (by local dissolution/reprecipitation); (ii) the increase in the crystallinity percentage of the main components (silica, alumina); (iii) tailoring the surface charge according to the use (e.g. negative homogeneous charge when heavy metals adsorption is planned).
- To allow all the surface reactions to reach equilibrium, this condition step must be developed over a long duration (48 h).
- The use of acids (HCl) or solubilizing agents (like Pyrocatechol violet or Complexone III) is not recommended as these will chemically react with the surface edges and corners, leaving very smooth surfaces, with low adsorption efficiencies.
- Alkali conditioning, with NaOH 1N, 2N and 4N solutions proved to meet all these targets; according to the adsorption results, the best substrate proved to be that obtained when using NaOH 2N.

2. Adsorption of dyes and heavy metals efficiently runs on fly ash conditioned with NaOH 2N

- This substrate proved to be highly efficient in heavy metals (cadmium, copper, nickel) removal even at very low concentrations (50 ppm), recommending this substrate for advanced treatment for water discharge/reuse, after a conventional treatment step (precipitation); a similar effect was registered for dyes (methyl orange and methylene blue).
- Selective adsorption is also possible as it was proved when investigating concurrent heavy metals adsorption: the copper cations are faster adsorbed with higher efficiency having the higher mobility and ionic degree of the copper tetra-hydrated complex, comparing to the hexa-complexes of Cd and Ni.
- Simultaneous removal of the methylene blue dye and cadmium, copper and nickel is possible on alkali modified fly ash (using NaOH 2N), the maximum removal efficiencies being reached after 60 min. of contact.

- The efficiency of the heavy metal adsorption which does not depend on the FA fraction used, becomes significant for the adsorption of large molecules, as it is MB or MO.

3. To increase reproducibility, fly ash surface can be conditioned with a dye thin layer

- Alkali modified fly ash (using NaOH 2N) develops a substrate with increased charge homogeneity after adsorbing methylene blue (MB).
- The MB-FA NaOH 2N represents a substrate with high affinity for copper and a moderate affinity for cadmium and nickel. The reason may be the higher mobility and ionic degree of the copper tetra-hydrated complex, comparing to the hexa-complexes of Cd and Ni, at the working pH of 4.8...5.3.
- Similar results were obtained when using methyl orange as surface modifier.
- Although these substrates are moderate, these experiments showed that dyes adsorption can run with the formation of strong bonds with the substrate, and this is was a conclusion that was used when investigating the simultaneous adsorption of heavy metals and dyes.

4. Efficient fly ash based composites can be developed with natural materials as bentonite or diatomite

- The alkali treatment raises sustainability issues therefore, the alkali fly ash may be replaced with washed fly ash (FAw) improved with washed powder bentonite (B) or diatomite (D), natural adsorbents with a composition almost identical to the fly ash.
- The removal efficiency of heavy metals and MB increases with the amount of bentonite in the composite, because the surface area of bentonite is larger than that of FAw.
- An important characteristic of the composite FA:B (1.5:0.5) is its large cation adsorption capacity, with convenient efficiencies after 90 min of contact time, that is not strongly influenced by the MB existent in the solution.
- The spent adsorbent annealed at 500 °C can be included in stone blocks resulting hybrid inorganic- organic composites. This can be a suggestion for reusing the spent adsorbent for padding in the stone blocks.

5. Adsorption on fly ash can be designed combined with an oxidative (photo) Fenton process, allowing simultaneous removal of heavy metals and dyes

- In testing fly ash as adsorbent for commercial dyes in industrial wastewaters resulted from a textile company it was outlined the effect of hydrogen peroxide in the process efficiency. Under UV-VIS radiation, adsorption and photocatalytic effects were running, with possible Photo-Fenton reactions due to the iron ions from FA. It was also showed that the fastest degradation corresponds to the dyes with the most rigid molecule (anthraquinone type) while the more flexible dyes are degraded slower.
- Following these findings, further tests were done on methyl-orange (MO) which proved to be one of the most difficult to degrade/adsorb dye.
- Removal efficiency of MO at two concentrations ($C_1 > C_2$) after 60 min adsorption process is followed by other process, probable the reaction between H_2O_2 and substrate forming new active species for MO degradation in photocatalytic conditions.
- In a system that contains photo-Fenton reagent, MO and cadmium, the concurrent processes are registered both on the substrate and in solution. Efficiencies are high after a certain induction time, confirming an *in situ* conditioning of the substrate (by MO adsorption).

6. Fly ash-photocatalysts composites represent multi-functional materials, able to simultaneously remove heavy metals and dyes in a single step process, involving photocatalysis and adsorption

- As the photo-Fenton systems combined with adsorption on fly ash may lead to an uncontrolled number of by-products, simultaneously photocatalysis and adsorption was designed based on composites containing fly ash and wide band gap semiconductors (TiO_2 , WO_3).
- Optimization studies targeted two aspects: (i) high adsorption and mineralisation efficiencies for heavy metals (in dark) and for organic pollutants (under UV irradiation); (ii) an optimise content, keeping the photocatalyst at the lowest value (as imposed by the process efficiency), considering the costs.

- Combination of the substrate alkali modified fly ash (with NaOH 2N) with a photocatalyst (TiO_2 or WO_3) can reach full removal of the dye and heavy metals over 90% efficiency.
- The results obtained in cadmium, copper removal from their solution or with MB/MO on substrates with different FA: TiO_2 ratios, showed the optimal ratios: FA: $\text{TiO}_2 = 3:1$ and FA: $\text{TiO}_2 = 2:2$.

7. Zeolite-type materials can be obtained starting from fly ash in mild hydrothermal processes (100 °C, 1 atm)

- The fly ash is a potential candidate for getting substrates with significantly higher specific surface and controlled surface charge, of zeolite type.
- The usual process is a rough hydrothermal synthesis. Through this research plan, zeolite type materials were obtained in mild conditions (100 °C and 1 atm)
- A new adsorbent material, FA-Z, was obtained from fly ash and was investigated as substrate for complex adsorption processes in a tri-component pollutant system, containing lead, zinc and cadmium cations. Based on mild hydrothermal treatment, fly ash is chemically altered to form a material having the $\text{SiO}_2/\text{Al}_2\text{O}_3$ over 2.4, with smooth and regular surface and with highly polar surface.
- Using the optimized adsorption parameters (contact time, ratio modified FA/mass: solution volume of initial pollutant concentration) the adsorption process were studied at room temperature, to evaluate the removal efficiency of heavy metals from wastewater with: (a) one, two and three heavy metals; (b) one or two dyes; (c) heavy metals with dye (methylene blue (MB) or methyl orange (MO)); (d) heavy metals with surfactants using FA with modified surface based on complexing agents and alkali hydroxide at different concentration, showed a limited adsorption efficiency of these type of material substrate.
- The adsorption studies proved that the novel material FA-Z is highly active in lead removal from mixtures also containing cadmium and zinc, on a broad concentration range and after a short contact time.
- The adsorption efficiencies on the novel FA-Z material were compared with similar data obtained using micro- and macroporous cation exchangers. Using the macroporous cation exchanger, the adsorption efficiencies are comparable with

those obtained on FA-Z, for all the cations. Lead removal on FA-Z is more efficient when compared also with the highly effective micro-porous cation exchanger. This recommends the new material for replacing the traditional synthetic ion exchanger in cation removal and especially in selective lead adsorption from mixtures containing more cations.

- Another novel substrate is obtained by hydrothermal processing of FA coated with a semiconductor, TiO₂ used for removing, in a single step process, heavy metals (Cd²⁺, Cu²⁺), and surfactants (cationic HTAB and anionic SDBS) from synthetic wastewaters containing two (heavy metal + surfactant) and three pollutants (two heavy metals + one surfactant).
- The substrate proves to be highly efficient in heavy metals adsorption and the TiO₂ layer on the fly ash grains demonstrates a good activity in surfactants photodegradation
- The negatively charged surface is also efficient in SDBS removal by photocatalysis with efficiencies up to 35%, this being a quite encouraging result as there were not used electron trappers.
- The kinetic and thermodynamic studies show that the substrate has a good adsorption capacity and fast adsorption processes are expected, mainly based on the electrostatic attractions between the substrate and the pollutant species.
- The new substrate has the grains in the micrometric range, representing thus a promising alternative to Degussa P25 slurries, allowing a simpler and cost effective method to recuperate/recycle the substrate in industrial wastewater treatment processes.
- The processes kinetic is studied and a conclusion was found that a pseudo-second-order equation describes well all the processes reactions. Large adsorption capacities are registered for heavy metals copper > nickel > cadmium, confirming its higher affinity for the substrate.
- Another possible kinetic model which can be applied in the adsorption on highly porous materials is the interparticle diffusion.

Original Contributions and Future Work

Through the research activities, there were formulated, developed and optimised several concepts with advanced degree of novelty, as:

- the association of two processes (adsorption and photocatalysis) in a “one step” wastewater treatment able to simultaneously remove inorganic and organic pollutants;
- the development of fly-ash based composites; using the micro-sized fly ash with embedded nano-sized TiO₂ photocatalyst, novel composites were obtained, active in simultaneous adsorption and photocatalysis (under UV irradiation). Additionally, these composites are easily filterable, which represent a pre-requisite for transferring these solutions at industrial scale;
- the development of zeolite-type materials, starting from fly ash in very mild hydrothermal synthesis conditions and of composites able to (partially) replaced the commercial photocatalysts.

A synthesis of the novel substrates developed within this research is presented in Table 61.

The validity of these concepts, proved on various types of wastewaters with complex pollutants load was proved by 24 publications in main stream journals, dedicated to materials science and catalysis.

The future will be dedicated to further investigations on:

- Optimizing the synthesis of zeolite-type materials, based on correlating the initial fly ash composition with the synthesis conditions.
- Developing solutions for immobilizing the mostly efficient substrates (mainly fly ash composites) as thin films or pellets.
- Developing novel solutions for integrated materials- processes - equipment for advanced wastewater treatment with complex pollutant load, targeting scaling up and market competitiveness.

Table 61. The substrates used in removing pollutants from wastewaters

Nr. crt.	Substrate	Pollutants			Efficiency in optimized conditions, [%]	Ref.	
		Heavy metal (HM)	Dye (MB, MO, industrial dyes)	HM+D/D+HM			Surfactant
(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)
1.	Fly ash-CET washed (FAw)	Cadmium (Cd ²⁺) Nickel (Ni ²⁺)	- -	- -	- -	1 g subs./100 mL solution; c _{in} = 0.01N, 60 min 1.78 10.58	[228]
2.	FA-CET- treated with HCl 2N	(Cd ²⁺)				- 17.31	
3.	FACET/Pyrocatechol Violet (FA/PV)	(Cd ²⁺)	-	-	-	- 16.14	
4.	FA-CET/ Complexone III (FA/CIII)	(Cd ²⁺)				14.82	
5.	FA-CET/Eriocrom Blacke T (FA/EBT)	(Cd ²⁺)				96.38	
6.	(FA-CET/NaOH 1N)	(Cd ²⁺)				92.99	
7.	(FA-CET/NaOH 4N)	(Cd ²⁺)				99.86	
8.	Activated carbon-powder PAC	(Cd ²⁺)				23.21	
9.	FA-CET/NaOH 2N (FA1/NaOH 2N) (FA1/NaOH:TiO ₂) 4:0; 3.9:0.1; 3.5:0.5; 3:1; 2:2	(Cd ²⁺) (Cu ²⁺) (Ni ²⁺)				>98 >99 >9	[228, 235] [235] [228, 235]
10.	FA-Mintia/NaOH 2N (FA2/NaOH 2N) 4:0; 3.9:0.1; 3.5:0.5; 3:1; 2:2	(Cd ²⁺) (Cu ²⁺) (Ni ²⁺)				>99 >90 >90	[235]
11.	FA- CET/MO/NaOH 2N (FA/MO/NaOH 2N)	(Cd ²⁺) (Cu ²⁺)				1 g/100 mL, c = 0.01N, 30 min 38.96 1 g/100 mL, c = 0.01N, 30 min 60.9	[224]
12.	FA-CET-2011 washed (FAw)	(Cd ²⁺)	-	-	-	70.02	[245]
13.	FA CET NaOH 2N (FANaOH)	Lead (Pb ²⁺) (Zn ²⁺)	-	-	-	1.5 g/100 mL; 60 min. 74.62 1.25 g/100 mL; 60 min. 32.39	[239]
	(FA-NaOH -MO)	(Pb ²⁺) (Zn ²⁺)				67.67 28.722	
14.	FA wood washed (Waw)	(Cd ²⁺)				2 g/100 mL; 30 min 99.990	[242]
15.	Bentonite (B)	(Cd ²⁺)				1 g, 90 min 50.32	[245]
16.	(FAw:B) 1:0; 0.5:0.5; 0.25:0.75; 0:1; 1:1; 1.5:0.5	Cd ²⁺ (Cd ²⁺ + Cu ²⁺) Cu ²⁺ (Cu ²⁺ + Cd ²⁺)				2 g/100 mL, 90 min 28.57-33.53 2 g/100 mL, 90 min 56.41- 81.92	[245]

Nr. crt.	Substrate	Pollutants				Efficiency in optimized conditions, [%]	Ref.
		Heavy metal (HM)	Dye (MB, MO, industrial dyes)	HM+D/ D+HM	Surfactant		
(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)
17.	Diatomite washed (Dw)	Cd ²⁺ Cu ²⁺				1 g/100 mL, 90 min 13.04 1 g/100 mL, 90 min 18.99	[250]
18.	(Dw + WAw + TiO ₂)	Cd ²⁺ Cu ²⁺				0.75 g/100 mL, 90 min 41.27 0.75 g/100 mL, 90 min 89.70	
19.	(TiO ₂)	Cd ²⁺ Cu ²⁺				1 g/100 mL; 60 min 5.36 1 g/100 mL; 60 min 11.79	[224]
20.	FA-CET/NaOH 2N FA1/NaOH:TiO ₂ 1:3; 1.5:2.5; 2.5:1.5; 2:2; 3:1	Cd ²⁺ Cu ²⁺				4 g/100 mL; 30 min 16.31-72.99 4 g/100 mL; 30 min 92.60 - 99.98	[249]
21.	FACET/NaOH 2N-TiO ₂ (FA/MO/NaOH:TiO ₂) 3:1; 2:2; 1.5:2.5; 1:3;	Cd ²⁺ Cu ²⁺				FA/MO/NaOH:TiO ₂ , 3:1:100 mL, after 15 min >89.00 FA/MO/NaOH:TiO ₂ , 3:1:100 mL, after 15 min >95	[224]
22.	FA CET (FA:TiO ₂ thin film) 4:1; 3:1; 2:2; 1.5:3.5; 1:3; 0:4		MB			thin film:25 mL; 360 min FA:TiO ₂ = 2:2 UV/H ₂ O ₂ system 40 UV/O ₂ system -85 UV/H ₂ O ₂ system	[252]
	FA CET (FA:TiO ₂ thin film) 4:1; 3:1; 2:2; 1.5:3.5; 1:3; 0:4		MO			FA:TiO ₂ = 2:2 >27 UV/H ₂ O ₂ system	
23.	FA CET FA-NaOH 2N		MB			1 g FA/NaOH : 25 mL 98.51 (F) 73.27 (A)	[257]
	(FA:TiO ₂) 4:1; 3:1; 2:2; 1.5:3.5; 1:3; 0:4		MB			93.07 (F) 99.95 (A)	
24.	(B+FA+TiO ₂) pellets		MB			1 pellet : 50 mL. 40.489 (A) Adsorption 65.691 (F) photo degradation	
25.	(FA:WO ₃) 0.5:1.5; 1.5:0.5	Cd ²⁺				- 2 g WO ₃ ; <0.00 (-20) at pH = 5.8 >20 pH = 8.3 >85	[254]
26.	(FA:WO ₃) 1.5:0.5			Cd ²⁺ (Cd ²⁺ + MB)		1.5:0.5, 3 g/100 mL; 60 min; i _{cd} < 300 mg/L >80	
	(FA:WO ₃) 1.5:0.5			MB (MB + Cd ²⁺)		60 min; 1.5 g FA : 0.5 g WO ₃ ; pH = 8.3 >60	
27.	(FA-M:TiO ₂)		MO			FA-M:TiO ₂ 34.85 FA-M:TiO ₂ substrates with H ₂ O ₂ ; 180 min 35.37 (A) 73.75 (F)	[259]
28.	FA CET washed (Faw)		MB			2 g/100 mL; 60-90 min 89.60 - 95.21	[242]

Nr. crt.	Substrate	Pollutants				Efficiency in optimized conditions, [%]	Ref.
		Heavy metal (HM)	Dye (MB, MO, industrial dyes)	HM+D/D+HM	Surfactant		
(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)
29.	FA wood washed (Waw)		MB			2 g/100 mL; 60-90 min 82.80 - 88.65	[242]
30.	(FA/NaOH 2N)		Industrial samples 1, 2, 3			2 g/100 mL-Vis; 120 min > 35 ; > 23 ; > 26	[167]
	(FA/NaOH 2N)		Industrial samples 1, 2, 3			2 g/100 mL; 120 min, UV > 15 ; > 14 ; > 28	
	(FA/NaOH 2N +TiO ₂)		Industrial samples 1, 2, 3			2 g/100 mL; 120 min, UV > 35 ; > 13 ; > 28	
31.	(FA/NaOH 2N)			Cd ²⁺ (Cd ²⁺ + MO) MO (MO + Cd ²⁺) Cu ²⁺ (Cu ²⁺ + MO) MO (MO + Cu ²⁺)		2 g/100 mL; 30 min 92.33 MO 0.025 mM 97.96 92.26 MO 0.025 mM 95.89	[160]
32.	(FA/NaOH 2N)			Ni ²⁺ (Ni ²⁺ + MB)		2 g/100 mL; 60 min 82.74	[226]
33.	(FA + CA) 1.75:0.25; 1.5:0.5; 1.25:0.75: 1:1; 0:2.			Cd ²⁺ (Cd ²⁺ + MB) MB (MB + Cd ²⁺)		2 g/100 mL; 30 min 1.95:0.25; 94.64 1:1; 44.89 0:2. 11.49 > 99	[251]
34.	(FA-CET) (FA:TiO ₂) 0.75:0.25			MB (MB + Cd ²⁺) Cd ²⁺ (Cd ²⁺ + MB) MB (MB + Cu ²⁺) Cu ²⁺ (Cu ²⁺ + MB)		1 g/100 mL, 30 min 96.74 (F) 96.16 (A) 99.99 (F) 99.96 (A) 94.71 (F) 97.28 (A) 99.94 (F) 98.05 (A)	[257]
35.	(FA-TiO ₂)			MO (MO + Cd)		Photo-Fenton 1.5 mL H ₂ O ₂	[259]
36.	(FA/NaOH 2N) 100 μm 200 μm	MB + (Cd + Cu + Ni)		Cd ²⁺ (Cd ²⁺ + Cu ²⁺ + Ni ²⁺ + MB) Cu ²⁺ (Cd ²⁺ + Cu ²⁺ + Ni ²⁺ + MB) Ni ²⁺ (Cd ²⁺ + Cu ²⁺ + Ni ²⁺ + MB) MB + (Cd + Cu + Ni)		2 g/100 mL; 60 min 100 μm - 12.99 200 μm - 17.32 100 μm - 88.74 200 μm - 79.20 100 μm - 7.92 200 μm - 64.92 100 μm - 62.09 200 μm - 46.77	[226]
37.	(FA-M-TiO ₂) (3 :1)			MO (MO + Cd)		4 g/100 mL Photo-Fenton 31.58-66.71	
38.	(FA-Z) (hydrothermal)	Cd ²⁺ (mixture)				0.5 g/100 mL; 90 min 15.60	[140]

Nr. crt.	Substrate	Pollutants				Efficiency in optimized conditions, [%]	Ref.
		Heavy metal (HM)	Dye (MB, MO, industrial dyes)	HM+D/ D+HM	Surfactant		
(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)
39.	C100 microporous	Cd ²⁺ (mixture)				41.83	[140]
	C100 macroporous	Cd ²⁺ (mixture)				19.64	
	(FA-Z)	Zn ²⁺ (mixture)				20.01	
	C100 microporous	Zn ²⁺ (mixture)				36.61	
	C100 macroporous	Zn ²⁺ (mixture)				22.17	
	(FA-Z)	Pb ²⁺ (mixture)				99.87	
	C100 microporous	Pb ²⁺ (mixture)				98.16	
	C100 macroporous	Pb ²⁺ (mixture)				64.28	
40.	FA/SDBS (FAA-CS24)	MB (MB + Cu ²⁺)				0.1 g/50 mL, 120 min 81.08	[267]
41.	FA/SDBS (FAA-CS48)	MB (MB + Cu ²⁺)				98.57	[267]
	FA/SDBS (FAA-CS24)	Cu ²⁺ (Cu ²⁺ + MB)				58.41	
	FA/SDBS (FAA-CS48)	Cu ²⁺ (Cu ²⁺ + MB)				60.25	
	FA/HTAB (FAA-CS24)	MB (MB + Cd ²⁺)				97.26	
	FA/HTAB (FAA-CS48)	MB (MB + Cd ²⁺)				84.97	
	FA/HTAB (FAA-CS24)	Cd ²⁺ (Cd ²⁺ + MB)				50.88	
	FA/HTAB (FAA-CS48)	Cd ²⁺ (Cd ²⁺ + MB)				44.96	
42.	(FA-TiO ₂) (hydrothermal)				SDBS SDBS (SDBS+ Cd ²⁺) Cd ²⁺ (Cu ²⁺ + SDBS) Cu ²⁺ (Cu ²⁺ + Cd ²⁺ + SDBS) Cd ²⁺ (Cd ²⁺ + Cu ²⁺ + SDBS) Cd ²⁺ (Cd ²⁺ + HTAB)	120 min; 0.25 g/50 mL 0.4 g/50 mL pH _{ads} = 4.96; pH _{UV} = 5.33 4.93 (A) 6.82 (F) 19.72 (A) 24.37 (F) 40.15 (A) 41.46 (F) 89.88 (A) 73.07 (F) 40.15 (A) 41.46 (F) 95.49 (A) 66.53 (F)	[129]

B.2. Career Development

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Department: Product Design, Mechatronics and Environment

The development of the university career and the future path proposed is outlined according to the long term national and European strategic objectives set for education and research in a knowledge-based society towards sustainable development.

The content of my university career is defined based on the two main tasks that characterize the activity in the academic area:

- Didactic, whose content and level is directly linked to the professional abilities of the graduates prepared for a global economy;
- Research in my field of competency, mainly contractual-based, as project coordinator and as team member in the Renewable Energy Systems and Recycling (RESREC) R&D Centre.

Both types of activities are in line with the University Strategic Plan and with the Managerial Plan of the Head of Product Design, Mechatronics and Environment Department, which promote preparing graduates for fast insertion in the socio- economic society and with a future strong contribution toward sustainable communities.

The didactic and research tasks are integrated developed: research involves students under different actions (team members in grants, diploma and dissertation subjects as part of the research activities); on the other hand, the teaching content is continuously enriched by adding the novel research results.

University Career Evolution

My didactic activity started in 1972 in pre-university education as Physics and Chemistry teacher. After the final exam in pre-university education, the main teaching subject was Chemistry as secondary school teacher, up to 2009.

During 2003-2009 my teaching activity was extended as associate lecturer in Transilvania University, Chemistry and Environment Department, focusing on topics of materials, chemistry and environment.

After obtaining the Ph.D. degree (in 2008) in Material Science, in 2009 I became associate professor in the Transilvania University, and in 2014 full professor.

This evolution had a very strong contribution to my progress in knowledge, teaching, in experimental work, in students' advice, in projects involvement.

The progress in my activity started by attending and promoting the two professional degrees, according to the pre-university hierarchy:

- 1986, teaching degree II in Chemistry (average mark 9.62);
- 1991, teaching degree I in Chemistry (mark 10).

The report developed for the teaching degree I, with the title „Interdisciplinary study in teaching - learning chemical kinetics” is a real guide in considering the Chemistry as a border subject with Physics, Biology and Mathematics, with a positive impact on understanding the chemical phenomena and on attracting pupils towards Chemistry.

As a general manager of the Natural Sciences College *Emil Racovita* in Brasov (2002-2007) and as head of the Chemistry Chair, I was deeply involved in organizing the teaching activities at institutional level, in infrastructure development for chemistry, physics, biology and informatics laboratories, increasing the quality of teaching and learning, supporting hands-on learning, and involving the institution and the appropriate teams in national and European projects.

After 2000, the progress in education was directly linked to ICT implementation in the teaching - learning and practical activities, developed by teachers and pupils. As teacher aiming at improving my knowledge in software and computer science, I attended the courses of Informatics organized in the Transilvania University, as part of a Tempus Project (2000-2002); consequently, as General Manager of the College, I promoted the ICT instruments (computers, software, training) in the school.

As a first result of involving ICT in teaching, I coordinated the development of a series of lectures in the field of organic compounds, to be implemented in the classroom by using novel tools: (i) Computer based development of the organic compounds structure; (ii) Computer based teaching and learning of chemical equilibrium. A paper was also developed and presented in the frame of the Symposium „Research and Methodology in Chemistry supporting the Education Reform in Romania,, (5th and 6th Editions, Predeal, 2000-2001).

In a next step, based on the experience gained and supporting the progress in teaching, learning and practical work in chemistry, I involved the school as partner in an European Comenius project, coordinated by the Transilvania University of Brasov, the Chemistry and Environment Department; the project was called „Chemistry Instruction Using Information and Communication Technologies - *CHEMNIC*” and was developed as the first pilot project of this type in Romania under the SOCRATES/COMENIUS 2.1. call, during 1999-2002. In this project, the main task I took over was training the secondary school teachers in applying ICT tools in chemistry. The first focus group consisted of teachers from my school, based on the experience I obtained during the mobility periods developed in Ghent University (Belgium) and SELETE Technical and Vocational Teacher Training Institute from School of Technical Educational of Patras (Greece).

The experience, the results and the novelty in chemistry teaching and training by extensively using the ICT tools are included in the book „Integration of Software into Chemistry courses” (Learning and Teaching Chemistry in Secondary Schools in the Society Informatics based) where I’m co-author.

During and after the project lifetime a wide dissemination process took place by using different instruments like reports, open lessons during the teacher workshops from Brasov

County, all of them in line with the Ministry strategy for promoting computer based teaching in the school.

Based on the experience and the positive impact of this European project on the staff and pupils from our school, I begun the action for a new Comenius project, as coordinator, in one of the specific subject: natural sciences. The project I coordinated was called „Water: Asset in the Sustainable Development of a joint Europe”, and run during 2004-2007; it had European schools as partners from: Italy - Lombardia - Istituto D’istruzione Superiore „Ciro Pollini”; Spain - Catalonia - les Frederic Mompou; Portugal - I Escola Secundaria; Turkia - Yzmir - Yzmir Ynonu High School. The central subject of this project is related to the water properties, quality, and social importance for the people. The project developed an integrated set of tangible products: the books „Clean water an Invaluable Asset” and „Glossary on water - properties and pollution” both in English language. The books were awarded the second place, in the school contest „Made for Europe 2008,, (Tg. Mures). Based on this project, a new teaching module „Water Chemistry” was outlined and introduced in the curriculum of the Emil Racovita College.

Further on, based on this experience I activated as mentor in training the teachers from the Brasov County and in the Izmir Inspectorate (from Turkey) in the frame of the Comenius project „Sustainable Energy for High School Education - an European Training Tool - *SEE - EU TOOL*”, coordinated by the Transilvania University, focusing on topics of Renewable Energy Sources and Systems.

This local, national and international didactic expertise allowed me to involve in coordinating students from the Physics - Chemistry study program in developing their projects.

Starting with 2003 I was involved in didactic activities in the Transilvania University of Brasov, Romania. During 2003-2008 my activity was focused on laboratory classes (Organic Chemistry, General Chemistry, Wastewater treatment), seminars (Organic Chemistry, Wastewater treatment) and in developing the didactic materials supporting these classes (laboratory sheets for practical activities on wastewater treatment and recycled materials for wastewater treatment).

In 2009 I applied for a full position as Associate Professor in the Transilvania University of Brasov, Faculty of Materials Science and Engineering, the Chemistry and Environment Chair. After following the legal steps (involving open competition), I became full time member of this structure.

The teaching activity during 2009-2014 included the following courses:

- Special materials / Recycled materials (diploma programs, Industrial Design and Wastes Engineering).
- Advanced materials and processes in wastewater treatment (master program Product Design for Sustainable Development and Environment Protection).
- Water treatment processes (diploma program, Environmental Engineering).
- Organic Chemistry (diploma program, Food and Tourism).
- General Chemistry (diploma programs in engineering).

The broad didactical experience gained in pre - university and university activities was also valorised by publishing books, in the Material Science and Environment Protection fields:

Visa, M. Wastewater Treatment Processes - Laboratory guide. Transilvania University Press, Brasov, 2014, ISBN 978-606-19-0353-5 (in Romanian).

Visa, M., Draghici, C., Dumitrescu, L., Nicolae, I., Patachia, S., Perniu, D. Technologies and Environment Protection, Transilvania University Press, Brasov, ISBN 978-606-5115-210-6 (in Romanian).

Visa, I., Duta, A. (editors). Sustainable Energy. Transilvania University Press, Brasov, 2008. The Chapter 4.2 - Waste (Water) Treatment - the author **Visa, M.** (the outcome of the project 226362-CP-1-2005-1-RO-COMENIUS-C21-SEE-EU TOOL).

Visa, M., Zanneti, V., Pereira, A., Esturk, E., Sancho, M., Clean Water - An Invaluable Asset, Transilvania University Press, Brasov, 2007, ISBN 978-973-598-031-3.

Visa, M., Zanneti, V., Pereira, A., Sancho, M., Esturk, E. Glossary on Water Properties and Pollution, Transilvania University Press, 2007, ISBN 978-973-635-989-7.

Spiliotopoulou-Papantoniou, V., Moraru, A., **Visa, M.**, Integration of Software into Chemistry courses (Learning and Teaching Chemistry in Secondary Schools in the Society of Information), Transilvania University Press, 2002, ISBN 973-635-047-9.

Evolution of the Research Career

In research, a novel subject at national level was opened through my Ph.D. program (beginning 2004), promoting the use of a waste product resulted in power stations - the **fly ash** - for advanced wastewater treatment, particularly focusing on waters resulted in industrial processes. This subject was extensively investigated through my doctoral program in Materials Science during 2004-2008, which was finalized with the thesis „*Adsorbent Materials with Controlled Surface Properties, Based on Solid Wastes, for Advanced Wastewater Treatment*”.

The main objective of the Ph.D. program was to develop novel absorbent materials, starting from fly ashes collected from the combined heat and power stations (CPH), and to optimize them as versatile substrates for the adsorption and photocatalysis of heavy metals and dyes, pollutants in industrial wastewaters.

In the doctoral thesis there were investigated the optimization conditions of single-type substrates based on fly ash and the properties of complex substrates obtained from fly ashes and TiO₂, optimized in terms of equilibrium duration and adsorbent mass/solution volume ratio in order to identify solutions that can be transferred and applied into wastewater treatment plants.

This period has contributed to my professional training in obtaining, synthesis and optimisation of advanced materials and gaining the skills to implement these into pilot advanced wastewater treatment processes. The extended laboratory research also allowed to get specific skills in the characterization of advanced materials in terms of: crystallinity, composition and structure (XRD, EDS, FT-IR), surface properties (AFM, SEM, BET, surface analysis, surface energy), optoelectronic properties (UV-VIS) and wastewater treatment (AAS, UV-VIS, TOC, TN).

After successfully finalizing the Ph.D. program I continued the research in the same field, through a post - doctoral program funded by the project POSDRU/89/1.5/S/59323. The subject of the post-doctoral project was „*Fly ash - based substrates for advanced treatment of industrial wastewaters*”, part of the research priority “*Innovative products and processes*”. This topic continued and expanded the doctoral program. Many papers coming from international groups confirm that adsorption is the method mostly used for pollutants removal from wastewaters, especially due to the good and controllable process efficiency, simple/already existent equipment, flexibility and low cost. Still, a quite limit number of low cost adsorption substrates proved to be efficient for industrial wastewater treatment: activated coal, clay, natural zeolites, ashes; common to these is the fact that they do not require special treatment before being used and can be embedded in inexpensive technologies; particularly interesting are the substrates obtained starting from wastes as second raw materials, as their use reduces the pollution burden as such and by involving in environmental depollution (as wastewater treatment). The novel concept introduced by the post-doctoral project was the development of composites of fly ash and photocatalysts for simultaneous removal of inorganic (heavy metals) and organic (dyes) pollutants in combined processes of adsorption and photo-catalysis. This concept was - to the best of our knowledge - for the first time formulated by our group and represented the focus of the three years project.

In the project, two main topics are subject of investigation:

- a) Development of materials: a complex system, active in simultaneous removal of organics (surfactants, organic dyes), and inorganic components (heavy metals), through photocatalysis and adsorption (under UV irradiation); the composite materials are based on nano-sized photocatalysts (TiO_2 , WO_3) embedded in micro-sized fly ash with modified surface; comparative studies were developed also using wood ash.
- b) Development of processes for advanced wastewater treatment: selecting and optimizing the process parameters in the simultaneous adsorption and photodegradation of organic and inorganic species from wastewaters with complex pollutants load (heavy metals, dyes, surfactants).

The results of this project met all the objectives formulated and got national and international validation through the published papers.

In the end of the post-doctoral period I applied and was granted the project “Novel adsorbents of zeolite type obtained from fly ashes collected from CPHs in Romania”, PN-II-RU-TE-2012-3-0177 contract no. 2/22.04.2013. The project is under development (2013-2016) and will investigate the correlations between the fly ash composition (and source) and the ability to form regular nano-structures of zeolite type. The results so far obtained show that there are significant differences between the fly ashes collected from CET Hunedoara-Mintia, CET Brasov, CET Craiova II and CET Govora.

During this period I also participated as team member in three other research projects, and the results of the research were disseminated through participation in six international and national Conferences, papers published in main stream journals, in conference proceedings, and a patent proposal.

Sensing the need for the development of young human resources for research, I coordinated the scientific activity of several students at the diploma and master works and together we published three papers in the Environmental Engineering and Management Journal, in the Proceedings of the Fly Ash Conference in Denver, and in Applied Surface Science Journal.

As part of the research activity and for increasing the visibility of the R&D center where I am working and of my university, I attended relevant conferences in Materials Science: Conference on Surfaces, Coating and Nanostructured Materials the Photocatalytic and Supercritical Surfaces Workshop, (Manchester, United Kingdom); European Materials Research Society E-MRS (Warsaw, Poland); European Meeting on Solar Chemistry and Photocatalysis: Environmental applications, SPEA (Prague, Czech Republic, Palermo, Italy); International Conference on Advanced Materials, ANM (Qingdao, China); Congress Fundamental of Adsorption (Kyoto, Japan); Fly Ash Conference (Denver, USA), etc.

International visibility gained during 2008-2014 is confirmed by:

- 24 ISI articles (17 as main author) published in journals with significant Impact Factor: Hazardous Materials (IF 3.925), Chemical Engineering Journal (IF 3.461), Catalysis Today (IF 3.407), Journal Applied Surface Science (IF 2.112), Adsorption - Journal of the International Adsorption Society (IF 2.0), Journal Clean Technologies and Environmental Policy (IF 1.753), Environmental Engineering

and Management Journal (IF 1.004), Journal of Sol-Gel Science and Technology (IF 1.632). Other papers are published in journals indexed in the Scopus database.

- 98 citations in ISI Web of Knowledge (without self-citations).
- Hirsch index $h = 7$.
- 15 papers published in ISI Conference proceedings.
- Scientific reviewer for the following ISI publications: Journal of Hazardous Materials, Chemical Engineering Journal, Material Science and Engineering B, Materials Chemistry and Physics, Central European Journal of Chemistry, Desalination, Journal of Catalysis, Applied Catalysis B, Environmental, Molecules, Applied Surface Science Journal, Environmental Engineering and Management Journal.

Proposal for the Career Development Plan

The Career Development Plan focuses on the research, education and management activities, and is developed considering the proven leadership skills, the results so far obtained in the teaching activity in the pre-university and university education, on the ability to propose and coordinate national and international grants and projects in the Materials Science topics, particularly in Advanced Materials for adsorption and photocatalysis.

General Objective

To continue, expand and capitalize the knowledge obtained in the research activity on advanced materials with adsorption and photocatalytic properties obtained based on the waste fly ash, for advanced wastewater treatment processes as well as to involve the students in the projects' teams and in the dissemination activities.

Didactical Activity Objectives:

- To continuously increase the quality of teaching in the study programs run in the Faculty of Product Design and Environment, Transilvania University of Brasov. This implies the continuous update of the didactic methods by including ICTs and multi-media, following the fast dynamics of these instruments, in teaching, learning and students assessment.
- To develop new teaching/learning tools: books, e-books, laboratory guides, to support the students in knowledge acquiring, mainly through project-based learning. These didactic tools will contain, at the appropriate complexity levels, novel findings coming from my research activity, being thus well suited for the study programs in Environment Engineering and Wastes Engineering.
- Guidance and tutorship for the students at diploma and master levels, focusing on the integrated approach material - product - technology, as part of their training for successfully accessing the labour market.

Research Activity Objectives:

- Increasing the visibility of the research results obtained in the department and university. A particular focus will be the development of links with industrial partners as part of up-scaling and transferability of the novel materials and processes.
- Attracting funds through national and international grants and contracts, also involving industrial partners.
- Continuous dissemination and networking through participation in relevant national and international scientific and technical events, focusing on advanced materials for environment protection.

One specific objective links the didactic and research activities and is the main reason for submitting the Habilitation Thesis. This objective is **to be directly involved, as Ph.D. coordinator, in the development of young human resources trained through and for research, in the field of Materials Science.**

Expected Results

In teaching:

- Improvement in the curriculum structure and in the content of the disciplines, aiming at quality education and student-centered programs.
- Promoting new study modules and new study programs, as an answer to the knowledge dynamics and to the requests of the labour market.
- Novel, modern teaching instruments and methods through ICTs, remote experiments, interactive teaching for increasing the students' participation and interest in the learning process, promoting team working, project-based and problem-based learning.
- Improved communication with the students, including the eLearning platform.
- Novel assessment methods, allowing the students to develop creative thinking and giving real value to the knowledge gained during the classes.

These results are expected to increase the attractiveness of our study programs, thus being able to increase the number of attendees joining our faculty and university.

In research:

- Continuously increased level and visibility of the research developed in the R&D Centre "Renewable Energy Systems and Recycling", in which team I am part of. The joint concept in the Center is "From Material to Prototype" and promotes interdisciplinary research for the development of novel, high-tech products.

- New interdisciplinary projects, involving the research groups in our Center (Advanced Materials and System Design), along with other relevant R&D entities and industrial partners. Following this concept, I coordinated a project proposal formulated in 2013 under the PNII Partnership call. The project proposal “*Innovative Integrated Materials - Technology - Equipment System for simultaneous photocatalysis and adsorption applied in sustainable wastewater treatment*” was evaluated and assessed with 94 points under the research priority *Innovative Products and Processes*.
- Novel equipment developed as demonstrators throughout the projects, in joint cooperation with the industrial partners, and implemented in the R&D Center for testing and optimisation. Also, according to the grant rules, the enlargement of the existing R&D infrastructure will be targeted.
- Increased visibility of the R&D Center through publications in main stream journals (ISI with significant impact factor and relative impact score).
- New patents with increased impact, to be applied in industrial products development.
- New books/chapters in books published in internationally recognized publishing houses.
- Increased visibility of the Conference for Sustainable Energy, organized each 3 years by the R&D Center where I am activating, by including sections dedicated to advanced materials for environment.
- Increasing the number of foreign students attending the International Summer School “Sustainable Metropolitan Regions of Tomorrow”, yearly organized by our R&D Center, by including topics related to advanced materials for wastewater treatment at community level.

These results will also support the development of Ph.D. programs under my coordination and the involvement of the doctoral students in a research group with coherent, interdisciplinary activity, and with a set of resources (human, infrastructure, partnership, national and international visibility) they can benefit on.

Conclusions

The experience and knowledge gained in my teaching and research activity in the field of novel materials for advanced wastewater treatment, along with the entire activity developed at pre-university and university levels have essentially contributed in defining my personality as teacher/professor and researcher and contributed to the national and international visibility in the scientific community.

This work and its results could and should represent the basis for developing a group focused on composites with tailored properties, fly-ash based, to be used as low cost, low energy, sustainable materials for wastewater treatment, targeting reuse. The development of doctoral programs and of projects within this group could contribute to the main research topic of our R&D center: renewable energy systems and recycling as a path for developing sustainable communities.

The activity and the plans for the future are fully in line with the Sustainable Energy Technologies (SET) Plan formulated by EU for the period 2014-2020 and with the Horizon 2020 priorities set within the pillar Societal Challenges: the rational use of resources, wastes recycling and advanced materials for energy saving and green energy production and use.

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