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Abstract of PhD Thesis

RESEARCHES ON THE REDUCTION OF WASTE WATER POLLUTANTS

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INTRODUCTION

PRESENT STAGE OF KNOWLEDGE

Chapter 1. The present stage of research regarding the methods of reducing waste water pollutants

1.1. Introduction

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1.3. The reduction of waste water pollutants from metal coating workshops that apply adsorption – ionic exchange processes

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PERSONAL CONTRIBUTIONS

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Electronic Microscopy

Chemical Analyses

X-ray Diffractometry

IP Spectroscopy

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3.1.1. Physico-chemical analysis of Valea Chioarului bentonite deposits

Macroscopic Analysis

X-ray Diffractometry

Electronic Microscopy

IP Spectroscopy

Chemical Analyses

3.1.2. Physico-chemical analysis of Petreşti bentonite deposits Macroscopic Analysis Chemical Analyses

3.2. Experiments

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4.1.1. Experiments

Obtaining the Fe-Zn-TVZ catalyser

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Obtaining the catalyst

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Cap.5. Final conclusions. Personal contributions

Bibliography

Annexes

II KEYWORDS: electroplating wastewater, Romanian bentonite, zeolitic volcanic tuffs, adsorption-ionic exchange, organic pollutants, Fe-Zn-zeolitic volcanic tuffs catalyst

III Short presentation of the thesis

The thesis is structured on five chapters that show the information as follows: (1) The treatment methods of waste water in metal coating industry, respectively of waste waters with hardly biodegradable components; (2) Experimental research on the elimination of iron and zinc ions from waste waters of electrochemical galvanization workshops through ionic exchange processes on zeolitic volcanic tuff from Pâglişa; (3) Researches concerning the retention of iron and zinc ions from waste water through bentonite adsorption from the deposits in Petreşti, Cluj County and the Valea Chioarului, Maramureş; (4) The reutilisation of residual volcanic zeolitic tuff in the case of obtaining a Fe/support type catalyst, and the testing of this catalyst during the process of degradative phenol oxidation in heterogenous Fenton-type process (5) Final conclusions that can be drawn from literature data as well as from experimental ascertainments done within the framework of the present doctoral thesis, original contributions.

In Chapter One a systematic material is presented compiled based on literature data, about the present stage of research in the controversial field of environmental pollution with inorganic and organic components.

The treatment of waste water is done through various physical, physico-chemical electrochemical, biological etc. methods. The present-day heavy metal ion retaining methods from

waste water are usually chemical ones based on transforming heavy metal ions into hardly soluble forms, precipitation or coprecipitation.

Given the fact that classical waste water treatment methods cannot bring the physical-chemical characteristics of water under the maximum limit values prescribed by existing legislation, the combination of water treatment procedures, namely the utilisation of classical procedures followed by the finishing of waste water by adsorption-ionic exchange, electrodialysis, etc. is imposed.

Literature data frequently reports new inorganic (natural zeolites, lava, clay minerals) or organic (micro-organisms - algae, bacteria, fungi, as well as various cellulosic materials) adsorbents with relatively low cost and which can be used for the finishing of residual waters containing metal ions. Natural zeolites and clay minerals (bentonite, kaolinite, vermiculite) have been used frequently for retaining heavy metals from residual waters. For example, clinoptilolite, which is the most frequent natural zeolite (with deposits in Italy, Croatia, Turkey, Greece, Romania), has been proven to be highly efficient in the process of retaining Zn^{2+}, Fe^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+} and Mn^{2+} ions. [34-88]

In metal coating industry, the tendency on a global level is to realise and use clean technologies in the closed system without waste and the recycling of all waste resulting from process bath regeneration, the minimisation of water consumption and the complete recycling of process solutions into washing waters of the instruments and devices, the recuperation of materials from solution leaks as well as from residual materials resulting from filtration.

Chapter two presents the research on the elimination of heavy metal ions (iron and zinc) from the depleted electrolytes of pickling and neutralisation baths at SC BETAK SA in Bistrita, through a process of ionic exchange using zeolitic volcanic tuff from the Pâglişa deposit in Cluj County. Zeolitic volcanic tuff samples were cropped out from a depth of two metres and characterised by modern methods (chemical analysis, optical and electronic microscopy, X-ray diffractometry, IR spectroscopy, etc.). These samples have been processed by physical and physico-chemical methods (grinding, sifting, washing, drying, acid treatment, alkaline treatment) in view of utilisation as ionic exchangers.

Depleted electrolyte samples have been processed by dilution respectively by neutralisation, filtration, dilution, with the aim of creating samples with neutral pH values, as well as the reducing of iron and zinc ion concentration, taking into consideration the fact that adsorption-ionic exchange processes are used in the case of the treatment of waste water with lower metallic ion contents. Within this chapter the following issues have been studied: influences of the granulation of zeolitic volcanic tuff samples, the optimal quantity of natural zeolite for the maximum yield in retaining metallic ions, the effect of the pH value of waste water samples, the

working regime (statical or dynamical) as well as the effects of zeolitic volcanic tuff treatment. The conclusion has been drawn that diffusive processes play an important role in the process of heavy metal ion retainment through ionic exchange, and maximum yields of the de ionic exchange processes (100%) were obtained in the case of zeolitic volcanic tuff samples with a granulation of 0,2-0,4 mm, in a dynamic regime. The pH value of residual waters has a special significance on the yield of iron and zinc ion retainment, as the maximum yields of ionic exchange were obtained in the case of residual waters with a neutral pH value.

Based on the experimental data, the adsorption isotherms of the iron and zinc ion retainment process on zeolitic volcanic tuff from Pâglişa were drawn, and establishing the fact that the adsorption of the two metallic ions occurs in accordance with the second-order kinetic model.

Chapter three presents the studies related to heavy metal (iron and zinc) ion retainment by adsorption on bentonite from the deposits in Petreşti (Cluj County), and the Valea Chioarului (Maramureş). The bentonite samples, cropped out from the two deposits, were analysed by various modern physico-chemical methods (macroscopic analysis, wet chemical analysis characteristic for silicaceous materials, optical microscopy, electronic microscopy, specific BET surface area, X-ray diffractometry, IR spectroscopy).

In the bentonite samples from the Valea Chioarului the massive presence of Na-montmorillonite was shown, as well as of halosit and caolinite (fractions < 2 μ), cristobalite, quartz and feldspath, the EDS spectrum of the bentonite samples indicated the presence of elements – Si, Al, Na and O – in the structure of the mineral, along with other elements, – K, Ca, Mg, Fe, Ti, Cu, and confirmed the fact that Valea Chioarului bentonite is a Na-montmorillonite type bentonite. The chemical composition of the bentonite samples has been determined by wet chemical analysis (specific for silicaceous materials), showing a high content of silicium oxides and a low content of iron oxides. Sodium oxide can be found in a larger concentration (ca. 2.2%) compared to other occurrences of bentonite in Romania (Oraşu Nou, Petreşti). The bentonite composition also included, aluminium oxide (13.90%), calcium (3.35%), as well as tracks of potassium, magnesium or titan oxides.

The experiments done regarding iron and zinc ion adsorption capacity from waste waters show that the bentonites from the two deposits, Petreşti and the Valea Chioarului have a high adsorption capacity. The adsorption yield of metallic ions was 100% after approximately 48 h in the case of zinc ions and 72 h in the case of iron ion (static regime). The heavy metal ion adsorption process in the case of the two studied bentonite types can be conducted in static and dynamic regime, by shaking; the disadvantage of using bentonite powders in the adsorption process of pollutants from waste waters is that it is not possible to fixed bed column, due to silting.

In Chapter four the reutilisation of residual zeolitic volcanic tuff has been proposed, used at the retainment of zinc and iron ions in the previous chapter, and the obtaining of a Fe/support catalyst. This catalyser was studied in the degradative phenol oxidation processes by heterogenous Fenton-type procedures (H_2O_2 and Fe-Zn-zeolitic volcanic tuff catalyst). Synthetic phenol solutions of a concentration of 1.33 g/dm^3 were used, the phenol in the present study being used as a model component as it is a non-biodegradable chemical component, which alters the organoleptical characteristics of the water (taste, smell), reduces the quantity of dissolved oxygen and it is a toxic, cancerigenic or mutagenic compound, being bioaccumulated in living organisms. The study followed the influence of catalyst quantities and the effects of temperature on the yield of the degradative oxidation process of the phenol and it has been determined that the oxidation yield of the phenol with Fenton reactive H_2O_2 and Fe-Zn-zeolitic volcanic tuff catalyst has large values (>90%). In addition to that this catalyser presents the advantage of significantly lower costs than those presently existing in the industry.

Chapter five present the conclusions resulting from the studied literature data regarding the depollution of waste water with heavy metal and organic pollutant contents, original contributions, as well as the directions of future research.