Research and development regarding the retaining mechanism of lead ions in industrial wastewaters using natural matter with remarkable properties

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Abstract. The paper shows the studying of the retaining mechanism of lead ions in industrial wastewaters through static and dynamic ion exchange mechanisms. In the experimental determinations of the lead metallic ion retention, metallurgical industry wastewaters have been used on samples of volcanic zeolite tuff (from Barsana, Maramures), samples that show a high concentration of lead ions and an acidic pH. The results showed that both the static and the dynamic ion exchanges ended with good results and they were consistent with other studies conducted on clinoptilolite zeolite tuff. Knowing that the industrial sector is an important source of environment pollution and degradation and being aware of what a serious threat the heavy metal pollution is, due to their high toxicity and stability, the experiment may find applicability in different aspects, both in the Maramures mining basing as well as in the worldwide controlling and directing of the polluting processes.

1. Introduction

The growing tendency of degrading the environment, the irrational management of natural resources as well as the zeolite applicability in various technological areas has led to the anchoring of the present research regarding the technological and economical process of the Sustainable Development Concept.

The natural zeolites are minerals with remarkable ion exchange proprieties, offering numerous application possibilities. The literature data shows concerns about using new inorganic adsorbents (natural zeolites, clay minerals), multiple studies conducted lately having shown a growing tendency in using them.

The ion exchange is a physical-chemical process used especially to eliminate heavy metal ions from watery solutions and it is based on the proprieties of some materials (natural zeolites) of replacing own ions with solution ions (wastewaters containing heavy metals).

The first methods used were the simple chemical precipitation or decomposition which were applied discontinuously, although, the wastewaters volume growth and the diversification of the contained pollutants led to the diversification of the methods and their continuous application.

A study conducted in the northern regions of Brazil which focused on the industrial waste usage when synthesizing the NAA zeolite showed that the temperature was maintained at a constant 110°C throughout the synthesizing process of the NAA zeolite and the durations and ratios of Na/Al were modified. The x-ray diffraction results (XRD) showed an elevated purity for the NAA zeolite, with a high structural order degree; according to the XRD results, which pointed the creation of the KA,
MGA and CAA zeolites, the cation exchange process between the NAA zeolite Na and solution K, Mg and Ca was efficient [1].

Arsenic adsorption on adsorbents like modified natural Ca-clinoptilolite zeolite and MnO2, was investigated in order to explore the feasibility of arsenic removal from underground waters using the adsorbent proprieties of natural zeolites. It was found that the amphoteric proprieties and the arsenic removal efficiency by using the natural Ca-clinoptilolite zeolite were improved significantly after the MnO2 modification. The removal efficiency obtained on the modified zeolite was doubled compared to the one obtained on the unmodified zeolite. The modified-MnO2-Ca-clinoptilolite zeolite seems to be a promising adsorbent for the removal of arsenic from water [2].

The capacity of the natural zeolite tuff for the removal of Pb ions from watery solutions was highlighted by tracking the effects of various parameters: the optimal adsorbent mass, the contact time, environmental pH, the lead concentration (II) and temperature. The maximum removal efficiency of 92% was reached at a 5 pH with a contact time of 25 minutes for 10g/solid-to-liquid ratio and an initial heavy metal concentration of 100mg/L [3].

The cadmium removal efficiency was studied like a function of the contact time, the adsorbent concentration, the pH and the adsorbent dose. The results showed that the cadmium removal was best described by the Langmuir–Freundlich isotherm. The maximum cadmium retention happened at an approximately 6.0 pH for materials.

Bulky organic pollutants, like pesticides and pharmaceutical residues found in used waters, are hard to remove using microporous adsorbents because of their size. The paper investigates zeolites hierarched as potential adsorbents for the removal of watery phase heavy organic pollutants. The obtained materials were fully characterized through X ray diffraction, N2 physisorption, elementary analysis, pyridine adsorption followed by FTIR. Thus, the collective proves that the hierarched zeolites show a higher adsorption rate and capacity than the microporous ones [5].

Na-Y zeolites made from local Egyptian kaolin were investigated for their adsorption proprieties in order to remove Methylene Blue (MB) from watery solutions. The influence of the chemical composition of the kaolin minerals and the surface proprieties of premade zeolite on the adsorption processes was studied. The effects of various parameters, like the particles surface and dimension, the initial MB concentration, contact time, the adsorbent concentration and subsequent adsorption cycles were examined. The adsorption capacities of the zeolite compared to the MB are influenced, mainly, by the zeolite particle dimension rather than the zeolite content [6].

In this research, Cu2+ ion exchange characteristics on natural clinoptilolite zeolite at 2 and 22°C are presented, in order to facilitate de development of a permeable reactive barrier (OEA) for the treatment of heavy metal contaminated waters from Antarctica. The negative effects of cold temperature on the performance of fixed bed will have significant implications for the design of a PRB natural zeolite for the treatment of heavy metal contaminated waters in Antarctica or in other cold regions [7].

Two natural zeolites, clinoptilolite and chabazit, had their mixed heavy metals (Pb, Cd, Cu, Zn, Cr, Ni and Co) contaminated effluents treatment performance evaluated. The effects of relevant parameters, like the chemical treatment, the metal concentration, the pH and the presence of the recurrent ions were examined. Chnoptilolite and chabazite showed different selectivity profiles for all the researched metals, with the exception of lead, for which both used zeolites acted exceptionally well [8].

Zeolite tuff (from Barsana, Maramures) was used in the Pb, Zn static ion retainment experimental determinations, using a ratio of 10g zeolite tuff/100cm3 of wastewater (taken from the slag-granulating basin of the metallurgical plant S.C. Romplumb S.A. Baia Mare). The wastewater initial concentration of metallic ions was of 3,806 mg Pb2+/l; 129,20 mg Zn2+/l. The evolution of the ion exchange process to retain heavy metal ions on three types of grain size of the zeolite tuff sample was followed: 0.4-0.2mm (G04); 0.2-0.12mm (G02); <0.012-mm (G012).

Clinoptilolite is predominant in the zeolite material used in the experiment and it was emphasized through the electronic microscope quality analysis (SEM) and the quantity analysis through spectral
analysis (EDX). Images of the grain surfaces and the chemical components EDX spectrum, with the help of the scanning electronic microscope (SEM) type JEOL JSM – 5600 LV, were made for the G012 S.C. Romplumb S.A. Baia Mare samples set. The zeolite tuff that was in contact with the wastewater got separated through filtration, and the sampling for the determination of the Pb and Zn ion concentration was made at an interval of 12 hours. The Pb and Zn ion concentration was obtained through atomic adsorption spectroscopy at a 5.90 pH value. The efficiency of the ion exchange process was monitored by means of ion exchange efficiency. For lead, ion exchange efficiency values of over 96% were obtained, the maximum value being 99.17% for the G012 sample set. The maximum efficiency value for the Zn ions, for which the concentration in the initial sample was high, was of 52.85% [9].

The usage of Barsana zeolite tuff in the static ion exchange processes for the wastewaters heavy metal ions removal led to good results which were consistent with the ones presented in the specialty literature [10-12].

The structural characteristics of the used zeolite tuff are close to the ones described in literature, like the tuff from the Maramures basin described by [13], [14]; the usage of this tuff for research led to good results regarding the ion exchange process.

The (lot and column) conducted experiments show higher adsorption capacities for ICZ compared to Z and they were generally lower in mixed metal systems than unique metal systems. The column adsorption data was well described by the Thomas model [15].

The heavy metal equilibrium series adsorption, meaning copper, zinc and manganese, from mongolian natural zeolite solution waste samples was made. Natural zeolites are capable of adsorbing and removing heavy metals from watery solutions. In some cases, the metal hydroxide precipitation influenced the adsorption results. The saturated adsorbed quantities of the heavy metals, estimated through the Langmuir equation, were almost the same amongst each other, but they grew along with the pH of the solution and the cationic exchange capacity of the natural zeolite [16].

ZT samples were characterized through XRD, XRF, BET and TGA analysis in order to examine the SO2 adsorption on the Jordanian zeolite tuff (ZT). The sorption process was realized in a fixed bed column, in various functioning conditions. A single SO2 measuring technique was used for this examination, which was the UIC sulfuric coulometer. Up until a temperature of 200°C the SO2 assimilation by the ZT proved to be rising along with the temperature and then it dropped at higher temperatures. The fact that the ZT drying, through conventional and microwave heating, had a considerable effect on the SO2 adsorption and the breakthrough time was also noted. Experimental data was obtained for the adsorption isotherms and it was noted that it followed the BET (Brunauer-Emmett-Teller) isotherm model. It has been found that the adsorption process is exothermic when it happens in nature. ZT can be regenerated and the initial adsorption capacity was kept after three cycles of regeneration [17].

The results of one research suggest that the adsorption/desorption of any class of compounds can be controlled by temperature operations. Adsorption isotherms were drawn for watery solutions of toluene, cyclohexane, o-xylene, benzyl alcohol, phenol and cyclohexanol in a humus, in combination with zeolite-acid at temperatures of 4, 14, 24 and 34°C and they were used to calculate the isosteric enthalpy (Δ_adsHi) and the isosteric entropy (Δ_adsSi) of the process. For hydrocarbon compounds, toluene, o-xylene, cyclohexane, and o-xylene, Δ_adsHi as well as Δ_adsSi were negative, the process being exothermic. Instead, for hydroxyl compounds, benzyl alcohol, phenol and cyclohexanol, Δ_adsHi and Δ_adsSi were positive, the entropy growth probably reflecting the water molecules release during the adsorption time.

A study was conducted that aimed to investigate the potential usage of the tuff as a matrix for ammonia removal in an intermittent biofilter flow (IBF), compared to the sand one. The sand filters and the tuff ones were characterized in relation to the respective total microbial biomass biofilms, the number and the diversity of the ammonia oxides and the ammonia removal efficiency. The microbial biomass/lg of tuff was significantly larger than that of the sand. However, the ammonia was removed immediately using the tuff filters, while the sand filter removal started only after ten days, even though...
ious adsorption isotherms have been obtained, using lead ions. Zeolite tuffs showed similar adsorption behaviors before and after the heat treatment, are characterized using electronic microscopy, mechanical testing, mercury intrusion, and pervaporation of a watery solution of 90% ethanol weight at 75°C. It has been found that the number of the ammonia oxidation bacteria (AOB) was higher in the sand filter. From a practical perspective, the tuff can be used as an effective matrix in IBF for ammonia removal, eventually by creating a more appropriate environment than the sand for bacteria activity. This study suggests an available and inexpensive matrix to produce high quality effluent biofilters IBF [19].

In another study, which aimed to analyses the lead ion removal capacity, from watery solutions in various conditions, of a natural zeolite tuff, various parameters like the optimal adsorbent mass, the contact time, the environmental pH, the lead ions concentration and the temperature have been investigated. On top of that, various adsorption isotherms have been obtained, using lead ions concentrations between 1mg/l and 200mg/l. For a 10g/l-solid-liquid ratio and a heavy metals initial concentration of 100mg/l, the maximum removal efficiency of 92% with a 5 pH at a 25 minutes contact time has been reached [20].

Four geopolymers have been synthesized through a NaOH activation of a mixture made of kaolinite (from Jordan or Ukraine) and filling material (zeolite tuff or silica sand). In order to monitor the reaction and to characterize the geopolymers phases, x-ray powder diffraction (XRD), Fourier transformed infrared spectrometry (FTIR) and nuclear magnetic resonance (MAS-RMN) have been used. The remaining kaolinite in every geopolymer produced sample clearly indicated an incomplete reaction. The 29Si MAS-NMR spectrum of the geopolymers revealed the presence of tetrahedral SiO4, while the 27Al MAS NMR spectrum revealed the presence of both tetrahedral AlO4 and octahedral AlO6. The XRD patterns of the geopolymers showed the formation of a new feldspar mineral. The replacing of the silica sand filling with zeolite tuff significantly improved the corresponding geopolymer’s specific surface area [21].

Some studies investigated the cadmium adsorption process from watery solutions, by using Na-zeolite tuff, Fe-zeolite tuff and carbonic material from HCL treated pyrolised sewage sludge. The results show that the adsorption mechanism is a physio-chemical adsorption on heterogeneous materials. In the kinetic studies, the Na and Fe modified zeolite tuffs showed similar adsorption capacities for cadmium but they were higher than the capacities for carbonic material [22].

The functionalization of the Y-zeolite (Faujasite) with the β-cyclodextrin (CD) was achieved by using 3-glycidoxypropyltrimethoxysilane (GPTS) as a coupling agent (linker). Two different strategic courses have been taken: the linker grafting to the β-CD and then carrying out the zeolite reaction or the zeolite linker grafting and then carrying out the β-CD reaction. The obtained materials were characterized in several complimentary ways, including: electronic microscopy with focalized ions scanning beam, spectrometry X-ray dispersive spectrometry, thermogravimetric analysis and differential thermal analysis (TG-DTA), infrared spectroscopy (FTIR) with the Fourier transform and Brunauer-Emmett-Teller analysis (BET). The first strategy led to better adsorption abilities than the second. These new materials can be potential adsorbents for the rehabilitation of the gaseous or aqueous effluents [23].

A study was conducted for the 4A zeolites radiolysis, containing various amounts of water, under 137Cs gamma radiations, focusing on the influence of the water charging ratio. The hydrogen production improvement compared to the bulk water radiolysis was attributed to the energy transfer from the zeolite to the water and to the structural organization of the water inside the zeolite. Both were observed separately with a maximum efficiency for the energy transfer at a loading ratio of about 13%, and with a maximum water structuring impact at a charging ratio of about 4% [24].

The proprieties of the tubular fibers and of the zeolite membranes before and after the heat treatment, are characterized using electronic microscopy, mechanical testing, mercury intrusion method and pervaporation of a watery solution of 90% ethanol weight at 75°C. It has been found that the continuous zeolite layers keep the original crack-free morphologic shapes after the heat treatment. On the other hand, the resistance to compression and the separation performance of the inner side of the NAA zeolite membranes were significantly improved by post-synthesis heat treatment at 240°C for 6 hours [25].

Gas detection is an important environmental issue for this century. Whatever the purpose, be it industrial emissions control or interior air quality supervision, the challenge remains producing
efficient detection systems at low costs, adapted to atmospheric conditions. There are studies which focus on the estimation of the microwave transduction technical viability for toluene detection. The sensors are based on zeolite powders, placed on co-planar structures tailored for microwave gamma frequencies [26].

Using advanced electronic transmission microscopy techniques, combined with X-ray powder diffraction and smooth X-ray adsorption structural measurements, the atomic structures of the HEU natural zeolite and two other ion exchange types of zeolites: Ag⁺ (Ag-HEU) and Zn²⁺ (Zn-HEU) have been investigated. In both ion exchange materials, the natural HEU zeolite charging was confirmed. For the Ag-HEU, Ag⁺ ions as well as clusters at the extra frame sites and Ag nanoparticles were confirmed.

A natural zeolite (Z-N), rich in clinoptilolite, was modified (Z-Al) through hydrated aluminum oxide incorporation, with the purpose of simultaneous removal of the ammonia and the phosphate. The incorporation of surface hydroxyl groups (~Al-OH) in the zeolite structure, as active groups for the removal of the phosphate, was characterized by acid titrations (pH PZC = 4.5 ± 0.2). A reduced capacity of regeneration cycles for the zeolite phosphate was observed [28].

Type A Ag- and Zn- liquid ion exchange modified zeolite samples were characterized by physio-chemical and thermal analysis. The resulted materials with improved physio-chemical proprieties are promising candidates for being used as coagulants. X-ray powdered diffraction, as well as the nitrogen adsorption rate show a good zeolite structure and texture conservation after the ion exchange [29].

Interconnected EMT, EMT/FAU and FAU zeolites have been synthesized and applied as additives of FCC catalysts for hydro-enhanced gasoline. The analysis of the physio-chemical proprieties of the synthesis catalysts by various techniques: XRD, N2 adsorption-desorption, HRTEM, SEM, showed that the catalysts with incorporated zeolites have large specific surface areas, pores and suitable acidities.

2. Materials and experimental method

For the determination of the lead ions retaining performances, wastewater from the granulating pool of the lead obtaining metallurgical plant from Baia Mare and a sample of zeolite tuff from Barsana, Maramures were used.

The efficiency of some Barsana tuff in the lead ions (from wastewaters with a lead ion quantity of 5.36 mg Pb²⁺/L) retaining process was studied. The static and dynamic ion exchange process was monitored.

The zeolite tuff samples were examined by using the Jeol JSM – 5600 LV electronic microscope and by EDX analysis. The zeolites appear to have the shape of clinoptilolite tabular crystals (Figure 1 & Figure 2), the majority of them having 2-10 µm, some of them reaching 35 µm.

Wastewater was analyzed for the determination of the lead ions concentration, this concentration being determined by mass spectrometry with inductively coupled plasma. The analysis was conducted at the Bucharest Chemical-Pharmaceutical Research and Development Institute.

Chemically untreated zeolite tuff (BN) and chemically treated tuff (Z-Na; noted with BT) with a 0.02 to 0.4 mm grain size and a solid ratio of 1:10 for static exchange were used. The sampling for the lead ions concentration determination was made once every 24 hours until the balance was reached. For dynamic exchanges, the experiments were conducted on a ionic exchange column of 45 mm diameter. 10g of zeolite tuff, a solution flow rate of 0.055 ml/s and gravitational flow were used. The probing was made once every 100 ml of effluent until the ion exchanger exhaustion.
3. Experimental Results

The experiments conducted for static exchange processes in a previous study [11], having the Barsana tuff as zeolite material and wastewater from the metallurgical plant led to the choice as the optimal alternative of a 10g zeolite tuff/100cm³ wastewater ratio for tracking the efficiency of the ion exchange.

The values of the lead ion concentrations were determined by mass spectrometry with inductively coupled plasma for each set of samples and they can be found in table 1. In the Figure 3 the variation of the static ion exchange process for the chemically treated (BT) and untreated (BN) Barsana zeolite tuff sample can be found, and in the Figure 4 the breaking curves for the dynamic exchange process of the two Barsana zeolite tuff can be found. The dynamic exchange experiments were made on
column in the conditions mentioned earlier, using wastewater samples containing 5.36 mgPb^{2+}/L, chemically untreated zeolite tuff samples (BN) and chemically treated tuff in alkaline form (BT). The presence of the heavy metals should entail special attention because of their toxicity even in low concentrations.

Table 1. The values of the time depending static ion exchange capacities for the two types of samples BT and BN

| Time, [min] | $C_i = 5.36$ mg Pb^{2+}/L | $C_i = 5.36$ mg Pb^{2+}/L |
|-------------|-----------------------------|-----------------------------|
|             | BT                          | BN                          |
| 0           | 0                           | 0                           |
| 24          | 0.051                       | 0.038                       |
| 48          | 0.052                       | 0.049                       |
| 72          | 0.054                       | 0.047                       |
| 96          | 0.053                       | 0.05                        |
| 120         | 0.053                       | 0.05                        |

Figure 3. The variation of the static ion exchange capacity obtained for the chemically treated (BT) and untreated (BN) Barsana zeolite tuff

Figure 4. The breaking curves of the chemically treated (BT) and untreated (BN) Barsana zeolite tuff samples in dynamic contact with the wastewater
In Figure 4, the different shape of the breaking curves for the two situations can be seen. Where the chemically untreated zeolite tuff sample was used, the breaking curve slope is a lot smaller, which points to the fact that the lead ions charge of the zeolite tuff takes place at a slower rate and the breaking of the zeolite tuff layer takes place later. Thus the breaking happens after 250 minutes when using chemically treated zeolite tuff compared to 280 minutes when using chemically untreated zeolite tuff.

4. Conclusions
The chemically untreated Barsana natural zeolite tuff used in the static and dynamic ion exchange processes leads to good results regarding the lead ions retention. For the dynamic exchange we can observe small differences between the two types of samples used for the experiment.

The values obtained from the breaking curves show that the BT zeolite tuff sample is exhausted after 250 minutes, while the BN sample is still active in the ion exchange process, thus more efficient. This is due to the small potential (concentration) difference, the ion exchange process speed being lower, meaning the speed limiting stage becomes the ion exchange reaction.

It is shown that for the static exchange experiments there are no significant differences between the two chosen samples (BT and BN).

The Barsana Maramures natural zeolite with remarkable proprieties due to its clinoptilolite content, was pointed out by various studies conducted by [13], [14] and considered to be a natural material used for wastewater heavy metals ion retention by [9-12] and it led to very good results for ion exchange processes.

Lead can be found in the environment on natural ways, but most of it comes as a result of human activities which lead to unwanted polluting processes that can have a serious impact on the health, the various effects of the lead intoxication on the human body being well known.

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