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Dear Reader,

The stabilized state of the natural environment, which existed millions of years before the first human precursors appeared on Earth, and now, it is beginning to change to slightly unstable. Inherent natural equilibrium is disturbed by human activity. He has the strongest and most productive tool - his brain and the ability to think. This human ability is enhanced by highly effective mutual communication between people. Unlike other animals and plants, man does not draw from his surroundings just as much as he needs for his own life, but he has created the great demands and requirements for life.

In terms of living standards, a person puts in his / her surroundings requirements that, as a living part of the natural environment, should not have. These include technical gains (cars, electronics, etc.) and various instruments, devices that enable and facilitate human existence in its artificially created environment.

The basic point of functioning of such an artificial environment and human civilization is the ability to produce objects for themselves to serve the requirements and needs. This ability is important, because civilization actually parasites on the nature of our planet, which is not at its perfection able to meet all the requirements of civilization.

After this finding, human society has created the ability to produce and has begun to exploit the nature only as an "infinite resource of raw materials and energy." In the last few decades people have come to realize that nature has come to a state in many ways, when it can not regenerate itself.

The regenerative capacity of nature is perfect, but it is not adapted to such rapidly changing and widespread harmful effects. Nature can regenerate, but it takes a long time that its dynamic human society is unable to provide.

Creating a new "ecological" attitude of man towards the environment is a very difficult, but necessary task to be understood as a long-term process that must touch upon each individual and his / her personality. This field is focused the activities of 8- th ICEEE 2017 - International Council of Environmental Engineering Education - "Technology of Environmental Protection".

Lenka Dubovická, editor

CON

CONTENTS

The influence of natural zeolite modification on zinc adsorption from synthetic solution

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***Abstract*—Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to the nature of cation exchange, natural zeolites exhibit high performance in adsorption of cations in aqueous solution. Surface modification using various chemicals can change the surface charge of natural zeolite, making it more efficient for cations removal from solution. In this study, powdered Slovakian clinoptilolite has been tested as sorbent for zinc removal efficiency. The aim of this work was to study the adsorption process of zinc from synthetic solution. The effects of modification technique and also other operating parameters as adsorbent dosage, initial concentration of metal ions and contact time were investigated by a batch adsorption technique. These tests and results are perspective for further assessment of possible application of natural zeolite in wastewater treatment originating from hydrometallurgical recycling of EAF dust.**

Keywords: adsorption; zinc; natural zeolite; modified zeolite

I. INTRODUCTION

The presence of trace metals in the aquatic environment has been of great concern because of their toxicity and non-biodegradable nature [1]. Zinc is released into the aquatic environment through several industrial activities, such as mining, metal coating, battery production and its use in paints, ceramics, wood, fabrics, drugs, sun blocks and deodorants [2]. Zinc is associated with short-term "metal-fume fever", nausea, diarrhoea, depression, lethargy, and neurological signs, such as seizures and ataxia. For the zinc toxicity in environment it is needed to effectively remove this metal from wastewater in order to ensure adequately treated effluent quality for various uses [3,4].

Therefore, a systematic study on the removal of zinc from wastewater is of considerable significance from an environmental point of view. A number of methods are available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption [5,6]. Adsorption process has been and actually is the most frequently applied method in the industries, and consequently the most extensively studied. Among the wide variety of ion exchangers, zeolites are a suitable choice as they have a large cation exchange capacity and an affinity for heavy metals. They are also beneficial as a low cost sorbents [7].

Each zeolite species has its own unique crystal structure and hence its own set of physical and chemical properties. These differences in the properties of zeolites are attributed to the differences in the geological formation of the zeolite sources. Therefore, every special zeolite material requires individual research [8,9].

The structure of clinoptilolite consists of three-dimensional grid which consists of Silicate tetrahedrite $(SiO_4)^{4-}$ each interconnected via oxygen atoms; the atoms of silicon are replaced by aluminum ions $(AlO_4)^{5-}$, creating a characteristic spatial structure with a significant incidence of cavities, interconnected by channels, in which metal cations, or water molecules are stored. The total volume of these cavities is 24 to 32 % [10-12]. General formula of clinoptilotite is $(Ca, K_2, Na_2, Mg)_4 Al_8 Si_{40}O_{96}.24H_2O$. The content of SiO_2 and Al_2O_3 is 65 – 71.3% and 11.5 – 13.1%, respectively. Clinoptilolite is widely used in agriculture, livestock farming, construction, environmental protection, cleaning water and gases and in various industrial sectors [8,11].

The main objective of this research is to evaluate the use of clinoptilolite, a kind of Slovakian natural zeolite, as a sorption material for removal of zinc ions from aqueous solutions. The specific objectives of this research are (1) determine the optimal modifications reagent for increase the sorption effectivity of zinc ions; (2) to find the effect of initial concentration and adsorbent mass on zinc removal by modified zeolite with NaOH; and to (3) examine kinetics and isotherms of the sorption of Zn^{2+} ions on modified zeolite with NaOH.

II. MATERIAL AND METHODS

The stock solution of zinc was prepared by dissolving $ZnSO_4.7H_2O$ in deionized water in concentration of 1g/l Zn^{2+} ions.

Preparation of sorbent

Zeolite as sorption material with grain size 1-2.5 mm, type *Clinoptilolite* was obtained from Zeocem a.s Bystré, Slovakia[10,11].

Original zeolite (ZO) and modified zeolites were used for zinc sorption from synthetic solution. Chemical modification of zeolites involved hydrothermal treatment at 80°C during 2 hours in solutions 2M NaOH (GZ/NaOH), 0.5M Na_2CO_3 (GZ/Na_2CO_3) and 0.25M H_2SO_4 – (GZ/H_2SO_4), during 2 hours. PZ/NaOH was grinded in powder and hydrothermally treated in 2M NaOH solution at 80°C for 2 hours. Zeolite (ZT) was physically treated by thermal activation at 120°C. After chemical and physical treatments were zeolites washed with deionised water, for 30 minutes and dried at 105°C.

Effect of parameters

Physical and chemical modification

0.1g modified zeolite was added into beaker with 50 ml of zinc solution with concentration of Zn^{2+} equal to 50.2 mg/l, and shaking for 20 hours.

Adsorbent dosage

The zeolite (PZ/NaOH) amount was varied from 0.1 to 2.0 g/50 ml at initial zinc concentration of 934 mg/l. Suspensions are shaken for 24 hrs at 20°C.

Contact time

The zinc solution (200 ml) with initial concentration about 100 mg/l of Zn^{2+} ions was stirred with 0.4g zeolites (PZ/NaOH) during 48 hrs. 5 ml of sample was collected at the time intervals of 3, 5, 10, 20, 30, 40, 60, and 90 minutes and after 48 hours.

Zinc concentration

Solution with initial zinc concentration in the range 44 – 967 mg/l with 0.1g PZ/NaOH was shaken for 24 hrs. After sorption, samples were filtered through and pH values were determined. The filtrates obtained were analyzed for zinc content by using AAS (Varian AA20+). Quality control testing includes experiments with blanks and duplicates. The removal efficiency (%) and the amount of adsorbed zinc ions (q_e) were calculated using the following formulae:

$$\mu(\%) = \frac{(C_0 - C_e)}{C_0} \times 100,$$

$$q_e = \frac{(C_0 - C_e)V}{m}$$

III. Results

Effect of modification by various physical and chemical ways on zinc uptake

The adsorption characteristics of any zeolite are dependent upon the detailed chemical/structural make up of the adsorbent. The Si/Al ratio, cation type, number and location are particularly influential in adsorption [12,13]. These properties can be changed by several chemical treatments to improve separation efficiency of raw natural zeolite. Acid/base treatment and salts impregnation by ion exchange are commonly employed to change the hydrophilic/hydrophobic properties for adsorption of various ions or organics [12].

For the purpose of increase zinc sorption uptake, different chemicals were used for activation the zeolite surface. Zeolites were hydrothermally treated at 80°C in solutions of NaOH (2M), Na_2CO_3 (0.5 M) and H_2SO_4 (0.25M) during 2 hours.

Physical treatment includes thermal activation in oven at 120°C during 24 hours. Last portion of zeolite was grinded to powder and then hydrothermally treated in NaOH, as previously mentioned.

The uptake capacities of zinc were decreased in order: PZ/NaOH (A) > GZ/NaOH (B) > GZ/Na_2CO_3 (C) > ZO (D) > ZT (E) > GZ/H_2SO_4 (F) (Fig. 1).

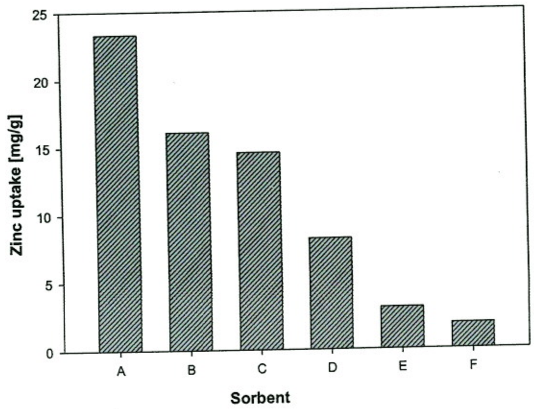

Figure 1: Zinc uptake over zeolites modified various ways (sorbent concentration = 2 g/l; Zn concentration = 50 mg/l; time = 20 h).

The highest sorption capacity 23.3 mg/g was reached with powdered zeolite hydrothermally pre-treated by NaOH. The same reagent used for activation of granulated zeolite caused the drop in uptake capacity about 31%, what represented sorption capacity 16 mg/g of Zn. The similar amount of removed zinc was reached by using of GZ/Na_2CO_3 (C) ($q_{(C)}$ = 14.5 mg Zn/g). The treating of zeolites by NaOH and Na_2CO_3 had positive effect on increasing in zinc removal from synthetic solutions. On the other hand, sulphuric acid used as chemical reagent and thermal activation causes strong decreasing of zinc uptake capacity. Zinc sorption capacity, 3 mg/g and 1.9 mg/g was obtained with ZT (E) and GZ/H_2SO_4 (F), respectively.

In general, acid washing of natural zeolite may remove impurities that block the pores, progressively eliminate cations to change into H-form and finally de-aluminate the structure [12].

Effect of adsorbent amount on zinc adsorption

The adsorbent dosage is one of the factors that also affect the adsorption process, since it determines the availability of active sites [14]. The effect of different adsorbent concentrations on metal ion removal is illustrated in Fig.2. The efficiency of zinc removal increases with increasing the amounts of adsorbent. This positive correlation between zeolite and removal was expected and could be due to the introduction of more binding sites and surface area[15]. The highest percentage of removed zinc from solution was about 60%, achieved with concentration of zeolite 40 g/l. However, the amount of metal adsorbed per unit mineral mass slightly increases adsorbent dosage up to 6 g/l and then sharply decreases. The highest adsorption capacity of zeolite was achieved with concentration of mineral mass 6 g/l, what presented 52 mg/g Zn^{2+}.

Some authors explain the effect of decreasing of equilibrium adsorption capacity with increase adsorbent dosage by un-saturation effect of some adsorption sites during the adsorption process. The second main reason is ascribed to particle aggregation resulting in a decrease of the total surface area and an increase of the diffusion path length [15-17].

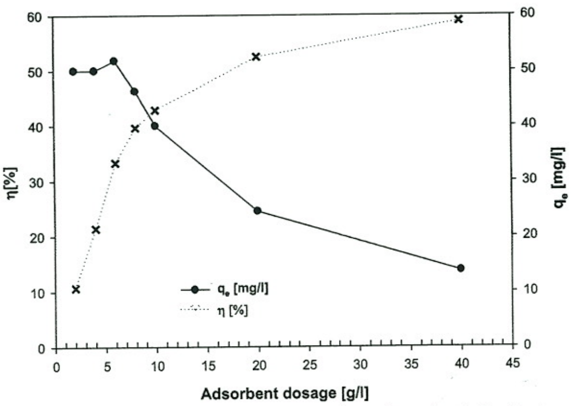

Figure 1: Effect of zeolite amount on zinc adsorption (adsorbent concentration = 2, 4, 6, 8, 10, 20, 40 g/l; Zn concentration = 934 mg/l; time = 24 h)

Effect of contact time on the zinc adsorption capacity

The time required for zinc sorption from synthetic solution by PZ/NaOH was determined as 90 minutes (Fig. 3). It was determined that the sorption rate is initially very fast. About 55% of zinc removal efficiency was achieved within the first 3 minutes. This short fast step of sorption is attributed to external occupancy of binding sites. Next step of sorption is ascribed to slow internal diffusion of zinc ions. Equilibrium was achieved after 3 hours of process and total amount of adsorbed ions of zinc was 80%. According to Alshameri et al. (2014), when the sorption of the exterior surface of the adsorbent reached the saturation point, the ions enter into the adsorbent pores and are absorbed by the interior surface of the particles [8].

Initial zinc concentration

The results of experiment is presented as a function of the different starting concentrations of Zn^{2+} ion as shown in Fig. 4; the increment in adsorption capacity was achieved in the ranges of 0-50 mg/L of zinc concentrations.

This observation is due to an increase in the mass transfer driving force resulting from the rise in initial zinc concentration. This can increase the rate at which Zn^{2+} ions move from the bulk solution onto the adsorbent. The result can be generally expected as clinoptilolite have micropores and macropores. With the zinc concentration above 50 mg/l, the removal efficiency of zeolite decrease. That is because the adsorbent tends to become saturated and a consequent decrease in the driving force required for further ion exchange of Zn^{2+} ion onto the zeolite. As a result, the Zn^{2+} could migrate from the external surface to the internal micro-pores of the zeolite within a given shaking time. Equilibrium was achieved when all the exchangeable zinc ions on the external and internal surfaces of the zeolite are replaced [8].

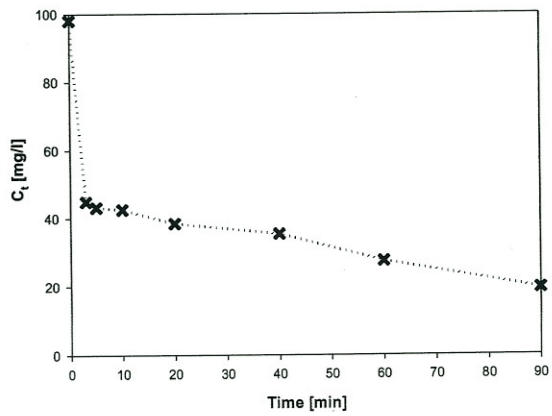

Figure 2: Effect of contact time on zinc metal ion adsorption (Concentration of PZ/NaOH = 2g/l, zinc concentration = 95 mg/l; Initial pH value = 6.28)

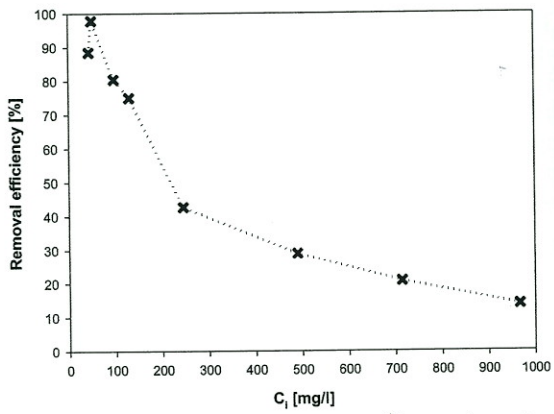

Figure 3: Influence of zinc concentration on Zn^{2+} removal capacity of the PZ/NaOH (contact time: 24 hours, 20 °C and pH 6.68 – 7.0).

IV. Conclusion

The removal of zinc (Zn^{2+}) metal ions from aqueous solution by zeolite was investigated. The following conclusions can be drawn based on this investigation:

- The modification of zeolite type clinoptilolite with NaOH has positive effect for sorption capacity of zinc as well as Na_2CO_3. On the other hand thermal activation and soaking in H_2SO_4 solution cause drop in sorption capacity for zinc ions.
- The kinetic of zinc sorption is rapid in the first 3 minutes and then followed by slower step.
- It was also found that the amount of Zn adsorbed per gram of adsorbent increases with the increasing contact time at all initial metal ion concentrations and equilibrium is attained within 90 minutes.
- With powdered zeolite activated with NaOH almost 100% of zinc was removed from the solution with initial metal concentration of 50 mg/l.

ACKNOWLEDGEMENT

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