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Editors

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ADSORPTION OF LEAD IONS FROM AQUEOUS SOLUTIONS USING CLINOPTILOLITE

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ABSTRACT: The adsorption of lead ions from synthetic aqueous solutions was performed by using natural zeolite (clinoptilolite). In order to determine the effectivity of clinoptilolite a series of experiments were performed under batch conditions from single ion solutions. Experiments were carried out at different initial concentration of lead ions, different initial pH values and different adsorbent mass.

The adsorption kinetics is reasonably fast. It means that in the first 20 min approximately 90% of Pb^{2+} is adsorbed from single ion solutions and equilibrium is achieved already after 20 min.

1. INTRODUCTION

Lead in small amounts (traces) occurs in soil and water. Higher lead concentration comes from industrial activities like mining (mine dumps, flotation tailings, acid mine water, etc.), metal industry, burning of fossil fuels, traffic. The main problem in industry is human exposure to lead. In case of toxic concentration, lead appears in the bone marrow, it can affect the process of hemoglobin production; it can participate in bone development instead of calcium, especially with six-year-old children because they are in a process of neurological and physical development. Acute intoxication can lead to kidney dysfunction, the reproductive system, the central nervous system and the liver [Zendelska, 2010].

Removal of lead can be accomplished by a variety of techniques. Conventional methods typically involve the use of processes such as coagulation, precipitation, ion-exchange, electro-chemical methods, membrane processes, extraction, adsorption, etc. Among these methods, adsorption is currently considered to be very suitable for

wastewater treatment because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of heavy metals include activated carbon [Kobya M. et al, 2005], clay minerals [Ammann, 2003], biomaterials [Sag Y. et al, 2000], industrial solid wastes and zeolites [Rajic N et al, 2010, Achanai et al, 2008, Çagin, 2006, Cabrera et al, 2005, Alvarez-Ayuso et al, 2003, Erdem et al, 2004, Gin, 2014].

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na^+ , K^+ , Ca^{2+} or Mg^{2+}) [Erdem, 2004]. Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalysts, mainly because zeolite exchangeable ions are relatively innocuous [Taffarel, 2009]. Thus, zeolites are particularly suitable for removing undesirable heavy metal ions (e.g. lead, nickel, zinc, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and

ammonium) from industrial, municipal and agricultural wastewaters.

2. EXPERIMENTAL

2.1 Adsorbent

The natural zeolite - clinoptilolite was used in the recent study as an adsorbent for adsorption of heavy metals, such as lead. The particle size range of the natural zeolite used in this study was 0.8 to 2.5 mm. The chemical composition of clinoptilolite are presented in (Table 1).

Table 1: Chemical composition of clinoptilolite samples

Chemical composition in % wt	
SiO ₂	69.68
Al ₂ O ₃	11.40
TiO ₂	0.15
Fe ₂ O ₃	0.93
MgO	0.87
MnO	0.08
CaO	2.01
Na ₂ O	0.62
K ₂ O	2.90
H ₂ O	13.24
P ₂ O ₅	0.02
ratio Si/Al	4.0-5.2

The sample was analysed on the content and type of exchangeable cations. The dominant ions, in the exchangeable position, is Ca²⁺ (67.14meq/100g) and K⁺ (41 meq/100g), followed by Na⁺ (16.10 meq/100g) and Mg²⁺ (3.88 meq/100g). The total cation exchange capacity is in the range of 1.8-2.2 meq/g.

X-Ray Diffractometer 6100 from Shimadzu was used to investigate the mineralogical structure of natural zeolite samples. The diffraction data obtained are compared to the database maintained by the *International Centre for Diffraction Data*, in order to identify the material in the solid samples. The results of XRD (Figure 1) showed that the natural zeolite contained clinoptilolite in the majority.

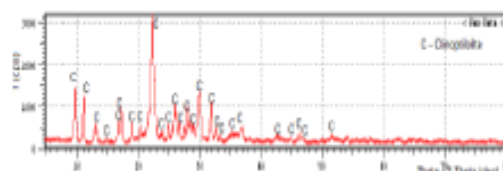


Figure 1: X-Ray diffraction of natural zeolite

The surface morphology of natural zeolite was studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is also fitted with a Inca 250 EDS system. EDS, stands for Energy Dispersive Spectroscopy, it is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X – Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons.

Micrograph of clinoptilolite sample obtained from SEM analysis is given in (Figure 2). The micrograph clearly show a number of macro-pores in the zeolite structure. The micrograph also show well defined crystals of clinoptilolite.

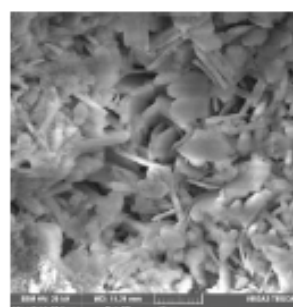


Figure 2: Micrograph of natural zeolite sample obtained from SEM analysis

The elemental composition of natural zeolite (clinoptilolite) is presented in (Table 2).

Table 2: EDS analysis for the elemental composition for natural zeolite

Element	%
O	57.56
Na	0.24
Mg	0.72
Al	5.28
Si	30.13
K	2.71
Ca	1.99
Fe	1.38
Total	100

Results of EDS analysis confirm that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure were K^+ and Ca^{2+} .

2.2 Adsorbate

The lead was used as adsorbate in the recent investigations. Synthetic single component solutions of Pb^{2+} were prepared by dissolving a weighed mass of the analytical grade salt $Pb(NO_3)_2$ in 1000ml distilled water.

2.3 Experimental procedure

Adsorption of lead ions on clinoptilolite was performed with synthetic single ion solutions of Pb^{2+} ions with different initial concentration. Initial pH of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting a mass of clinoptilolite with a certain volume of Pb^{2+} ions solution. Clinoptilolite sample and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was varied up to 120 minutes. At the end of the predetermined time, the suspension was filtered and the filtrate was analyzed. The final pH value was also measured. All experiments were performed at room temperature on $20 \pm 1^\circ C$. The initial and remaining concentrations of metal ions were

determined by Liberty 110, ICP Emission Spectrometer, Varian.

Based on material balance, the adsorption capacity was calculated by using the following expression:

$$q_e = \frac{V(C_0 - C_e)}{m}, (mg/g) \quad (1)$$

where: q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and final metal ion concentrations (mg/l), respectively, V is the volume of the aqueous phase (l) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$AD\% = \left(1 - \frac{C_e}{C_0}\right) \cdot 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Effect of initial solution concentration

Single component solutions 400ml were mixed with 5 g clinoptilolite and agitated for 120 minutes at the temperature $20 \pm 1^\circ C$ and pH value 3.5. The concentration of the single component solution was 5, 25, 50, 200 and 400 mg/l of Pb^{2+} . The results of the kinetic experiments to measure the adsorption of cations from aqueous solutions onto clinoptilolite as a function of initial concentration of Pb in solution and time are shown in Figure 3.

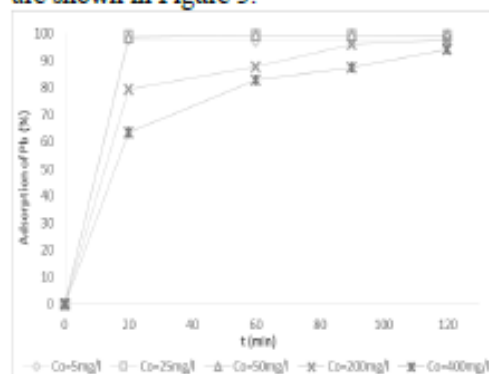


Figure 3: Effect of initial Pb^{2+} concentration on the adsorption of clinoptilolite

Table 3: Effect of initial solution concentration on the adsorption capacity of clinoptilolite

Initial Concentration C_0 (mg/l)	Amount Adsorbed q_e (mg/g)	Percentage Adsorbed (%)
5	0.392	97.6
25	1.991	99.2
50	3.987	99.54
200	15.642	97.76
400	30.143	94.19

The above results indicate that the amount of lead adsorbed by clinoptilolite at equilibrium is not dependent on the initial lead concentration. An increase in concentration not results with significant increases of the amount of lead adsorbed but affect in the rate of adsorption. At lower initial concentration equilibrium is reached already after 20 min, but when it comes to a concentration of 200 and 400 mg/l, equilibrium is achieved after 100 min. Higher initial concentration result with slower adsorption process.

(Table 3) also reveals that an increase in initial concentration results in an increase in the amount adsorbed (q_e). The adsorption capacity increase with an increase in initial concentration until the system reaches a saturation point, at which point further increase of the adsorbate (lead) concentration will not result in any significant change in the amount adsorbed, q_e .

3.2 Effect of adsorbent mass

A series of kinetic experiments at different adsorbent masses, that are, 2, 5 and 10 g, were performed using fixed initial metal concentrations for the lead cation (5 mg/l). The other conditions were 400ml solution agitated for 120 minutes at the temperature $20 \pm 1^\circ\text{C}$ and pH value 3.5.

The plots of the amount of metal adsorbed versus time are shown in (Figure 4).

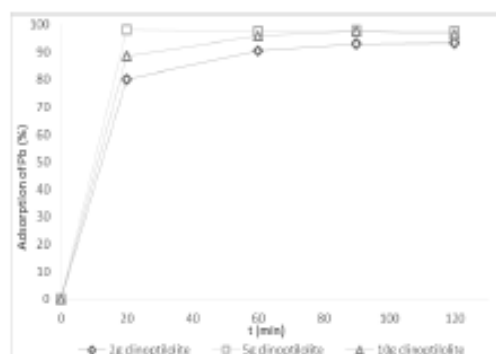


Figure 4: Effect of adsorbent mass on the adsorption of clinoptilolite

According to the percentage of lead adsorbed from solution, we can see that an increase in adsorbent mass resulted in an increase in the adsorption of the lead, but little, almost insignificant (Table 4). This is because as adsorbent mass increases more adsorption sites are available per unit mass of adsorbent added.

Table 4: Effect of adsorbent mass on the efficiency of natural zeolite for the removal of lead from solution

Adsorbent Mass (g)	Percentage Adsorbed (%)
2	93.2
5	97.6
10	96.4

3.3 Effect of initial solution pH

A series of kinetic experiments at different initial pH values 2.5, 3.5 and 4.5 were performed using fixed initial metal concentrations for the lead cation (5 mg/l) and adsorbent mass (5g). The other conditions were 400ml solution agitated for 120 minutes at the temperature $20 \pm 1^\circ\text{C}$.

The pH of the solution in contact with clinoptilolite has an obvious impact on its

ability to remove metals since the acidic solution can influence both the character of the exchanging ions and the character (structure) of the zeolite itself. In this investigation lead did not confirm that. (Figure 5) show that as solution pH decreases, lead removal efficiency not decreases, the efficiency stay constant.

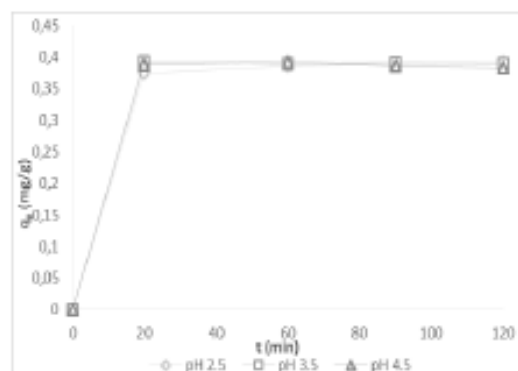
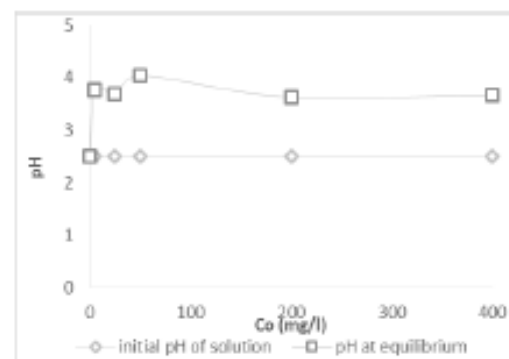
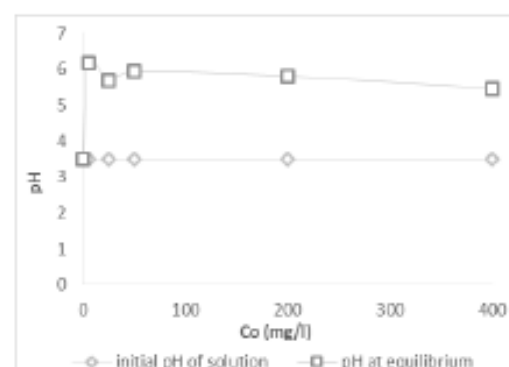


Figure 5: Effect of initial solution pH on the adsorption of clinoptilolite

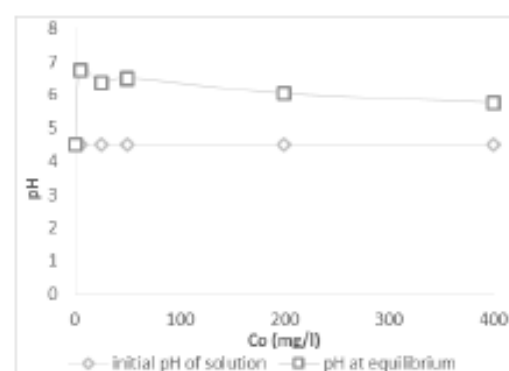
In addition, equilibrium pH change with respect to various initial lead concentrations is followed. The initial solutions were at different pH values.



a)



b)



c)

Figure 6: Equilibrium pH change with respect to various initial lead concentrations: a) Initial pH is 2.5
b) Initial pH is 3.5 c) Initial pH is 4.5

(Figure 6) presents the variation in the equilibrium pH values with respect to initial lead concentration in each equilibrium study. The equilibrium pH values are greater than the initially

adjusted pH values and the difference between equilibrium pH and initial pH exhibits a descending trend with increasing initial lead concentration. The increase in pH is a result of the adsorption of H^+ ions from solution, but as the initial concentration of lead increases, the concentration driving force begins to favour the adsorption of Pb^{2+} ions in preference to H^+ ions, and thus the descending trend of the equilibrium pH at higher initial lead concentrations.

4. CONCLUSION

The adsorption of lead ions from diluted solution onto clinoptilolite occurs efficiently.

The amount of lead adsorbed by clinoptilolite at equilibrium is not dependent on the initial lead concentration while the rate of adsorption depends. It means that higher initial concentration result with slower adsorption process. Effect of adsorbent mass on the adsorption of clinoptilolite is almost insignificant. An increase in adsorbent mass resulted in little an increase in the adsorption of the lead. According to initial solution pH can be concluded that in interval from 2.5 to 4.5 the efficiency for adsorption of lead from the solution by clinoptilolite is constant. The adsorption kinetics is reasonably fast. It means that in the first 20 min approximately 90% of Pb^{2+} is adsorbed from single ion solutions and equilibrium is achieved already after 20 min.

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