



Lead pollution removal from water using a natural zeolite[#]

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Abstract: Lead (II) ion adsorption capacity of clinoptilolite from artificial polluted tap water was investigated in this study. For the experimental studies, Clinoptilolite mineral which is 25-140 mesh size was used by activating with HCl, and lead ion removal efficiencies were examined. Experiments were studied under laboratory batch conditions were run at different pH values, temperatures. The highest removal efficiency was found as about 87% at pH 5. Similarly, experiments were carried out at different temperature values, and the maximum efficiency was obtained at 30°C. The efficiency obtained under these conditions was 89.95%. The highest lead removal efficiency was obtained with 200 rpm shaking speed.

Keywords: Heavy metal, lead, adsorption, zeolite, clinoptilolite, removal.

Introduction

Lead ions in the heavy metal pollution are one of the important environmental problems in the aqueous system originated from industry. Generally, heavy metal containing wastewaters have low biological oxygen demand and are very high toxic for micro-organisms responsible for biological oxidation of organic matter. There are many heavy metals produced from the industry that lead may be found a lot of industrial wastewater. Heavy metal pollution exists in many industrial wastewaters, such as metal plating facilities, mining operations, nuclear powerhouses, fertilizer industries, paints and pigments, municipal and storm water run-off, battery and tannery industries (Patterson, 1977). Some metals associated with these activities are as follows; lead, cadmium, copper, chromium *etc.* Heavy metals are not biodegradable and tend to accumulate into living organisms, causing various diseases and other problems. Lead and its compounds are found frequently in surface water, because it is a ubiquitous metal in the environment.

The most widely used methods for removing metal ions are as follows; precipitation with chemical and electrochemical methods or sometimes using sulphides (Chen., 2004; Marani *et al.*, 1995; Patterson, 1985). A major problem with this type of treatment is the disposal of the precipitated wastes. Ion exchange treatment which is the second most widely used method for metal ion removal does not present a sludge disposal problem and has the advantage of reclamation of Cu (II) (Petrus & Warchol, 2003). This method can reduce heavy metals to very low levels. However, ion exchange treatment does not appear to be economical. Activated carbon is also efficient for removal of trace elements from the waste water, but its high cost has prevented its wide usage. The adsorption phenomenon has still been found economically appealing for the removal of toxic metals from wastewater by choosing some adsorbents under optimum operation conditions.

It has been reported that some aquatic plants (Volesky *et al.*, 2003; Axtell *et al.*, 2003), agricultural by-products (Argun *et al.*, 2007a; Argun *et al.*, 2005; Ricordel *et al.*, 2001), sawdust

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(Özdemir, 2005), clay (Márquez *et al.*, 2004), zeolite (Álvarez-Ayuso *et al.*, 2003), turba (Twardowska and Kyzioł, 2003; Ho *et al.*, 1995) and microorganisms (Li *et al.*, 2004) have the capacity to adsorb and accumulate heavy metals. Cost comparisons are difficult to make due to the scarcity of consistent cost information. Although many experiments have been accomplished in the area of low-cost sorbents, a great deal of work is necessary to understand better low-cost adsorption processes and to demonstrate the technology.

Natural zeolites have ion exchange and removal capacity. Clinoptilolite has high removal capacity of metal ions Pb^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Ni^{+2} , Fe^{+2} and Mn^{+2} . Clinoptilolites exist at Balıkesir, Bigadiç and Gördes in Turkey. It is an economical ion exchange material comparing with the synthetic resin.

Natural zeolites have been used as adsorbent and ion exchanger with discovering crystal feature and some chemical structure. It is physical structure look like a selective sieve and named as molecular sieve by Mc Bain (1932). Ion exchange capacity of some zeolites is given in Table 1.

General formula of the Zeolites is $X[M^{+}_1, M^{++}_{1/2}](AlO_2)_ySiO_2 \cdot zH_2O$. M is a cation (Na^{+} , K^{+} , Ca^{++} , Pb etc.) which ratio (y/x) changes from 1 to 5. M^{++} is a cation (Ca^{++} , Mg^{++} and Ba^{++} etc.) change with M^{+}_1 . SiO_2/AlO_2 molar ratio or ratio (y/x) zeolite changes with zeolite types from 1 to 5.

SiO_4 and AlO_4 octahedra are the monomers of the zeolites that Si or Al was centre of the structure and oxygen was on the corners.

Table 1. Ion Exchange capacity of some zeolites (Hanson, 1995)

MINERAL	CHEMICAL COMPOSITION	Ion exchange capacity (meq/g)
Analsim	$Na_{16}(Al_{16}Si_{32}O_{96}) \cdot 16H_2O$	4.54
Lavmontit	$Ca_4(Al_8Si_{46}O_{108}) \cdot 16H_2O$	4.25
Natrolit	$Na_{16}(Al_{16}Si_{24}O_{80}) \cdot 12H_2O$	5.26
Mordenit	$Na_8(Al_8Si_{40}O_{96}) \cdot 24H_2O$	2.29
Flipsit	$(Na, K)_{10}(Al_{10}Si_{22}O_{64}) \cdot 24H_2O$	3.87
Eriyonit	$(Na, K, Ca)_9(Al_9Si_{27}O_{72}) \cdot 27H_2O$	3.12
Shabazit	$(Ca, Na)_6(Al_{12}Si_{24}O_{72}) \cdot 40H_2O$	3.81
Klinoptilolit	$(K_4Na_4)(Al_8Si_{40}O_{96}) \cdot 24H_2O$	2.54

Zeolite potential of Manisa-Gördes, operating by M.T.A (Mine Technical Search Institute), is 20 million tonnes reserve capacity. Balıkesir-Bigadiç has 500 million tonnes zeolite reserve capacity and total zeolite capacity of Turkey is 50 billion tonnes (Anonym, 1996). Clinoptilolite, mordenite, shabazite and filipsit etc. natural zeolites were used for removal of NH_4^{+} ion due to its low price and providing easily. Specially, clinoptilolite gave high performance, and have been used for treatment of liquid wastes. Natural zeolites were also used at industrial fish ponds (Ames, 1967). Chelischev (1974) used clinoptilolite as ion exchanger for heavy metals. Similarly Sato and Fukagawa, 1976 used clinoptilolite for nitrogen removal at detergent industry waste water.

The aim of this study was removal of the ionic lead pollution from the preliminary treated water using clinoptilolite as a natural and economical material.

Materials and Method

In this study, Beyköy region clinoptilolite was used provided from Susurluk town of Balıkesir city in Turkey. Its chemical analysis showed that it is member of hydrated alumina-silicate mineral containing mostly alkali and soil alkali metals originated in holes of volcanic

rocks. They contain hydrate in holes connected each other. Chemical composition of the clinoptilolite is given in Table 2. Particle size is 50-2000 μ of 82.56% materials and 2-50 μ others. Porosity ratio was about 50% and natural hydrate capacity and ion exchange capacity were 25.68 % and 71.73 meq/100g respectively. Materials used in this study were between 25-140 mesh sizes.

Table 2. Special composition of the clinoptilolite used in this study

		Useful Microelements (ppm)	Heavy Metal	and
Colour (dry)	5Y 8/1 (White)	Fe	2.33	
Colour (wet)	5Y 6/3 (Light olive)	Cu	0.032	
Sand (%)	82.56	Zn	0.31	
Clay (%)	3.44	Mn	2.34	
Silt (%)	14.00	Total Elements		
Structure	Silty sand	SiO ₂ (%)	70.05	
Density	2.14 g/cm ³	Al ₂ O ₃ (%)	9.84	
Volume weight	1.10 g/cm ³	Fe ₂ O ₃ (%)	0.96	
Porosity (%)	48.47	CaO (%)	2.15	
Natural hydrate capacity (%)	25.68	MgO (%)	0.58	
Colourless point (%)	23.24	Na ₂ O (%)	0.24	
Useful hydrate (%)	2.44	K ₂ O (%)	1.44	
Humidity (%)	5.84	MnO (%)	0.05	
pH	7.62	Pb ₃ O ₄ (%)	0.0014	
Total Salt (%)	0.03<	ZnO ₄ (%)	0.0044	
CaCO ₃ (%)	1.25	Cu (ppm)	1.56	
Org. Matter (%)	0.34	Zn (ppm)	34.95	
Total Nitrogen (%)	0.0084 (84ppm)	Cd (ppm)	0.09	
Useful Phosphor (%)	0.0068 (68ppm)	Ni (ppm)	4.25	
Cation Exchange Capacity (me/100g)	71.73	Co (ppm)	0.43	
Changeable Cations (meq/100g)		Cr (ppm)	2.36	
Ca ⁺⁺	21.00	Mo (ppm)	trace	
Mg ⁺⁺	12.00	Fire lost (%)	14.06	
Na ⁺	11.52			
K ⁺	27.18			

Gallenkap (U.K.) thermostatic shaker incubator was used for batch experiments. Lead concentrations were measured by Dr. Lange Cadas-200 Spectrophotometer (Germany). The pH was adjusted to required values using *Jenway 3010* pH meter. *Gec-Avery VA/WA* Analytical Balances was used to weighing procedure for preparation of solution.

Clinoptilolite in 25-140 mesh size was treated with acid or base solution in different concentration to improve its adsorption capacity. For this process, 2.0 grams of clinoptilolite in 100 ml distilled water containing different amounts of acid or base was shaken at different shaking speed and temperature, and finally 1 h 200 rpm and 23 h 100 rpm at 30 °C stable temperature. Seven Erlenmeyer I was taken which 3 of them contain alkali and 3 of them acid solution, and one is control. Then they were placed in a thermostatic shaker. Clinoptilolite samples were washed twice with distilled water after treating with acid or alkali solution. With this procedure, the best activation media was determined 2.0 ml 1 M HCl additions. For this reason, activated Clinoptilolite samples with 2.0 ml 1 M HCl were used in following experiments. After designing the activation media, to optimum adsorbent amount, each 2 grams of activated clinoptilolite was added in 100 ml tap water containing different concentration of Cu²⁺. After 1 h contact time in batch reactor, clinoptilolites were filtered with fine nylon filter and Pb²⁺ concentrations were measured using Curvette test via Cadas 200 UV-Vis spectrophotometer. Effect of pH on the adsorption capacity of 2 grams of clinoptilolites was tested adjusting pH of the 100 ml sample solution (containing 40 mg-lead/l) via adding different amount of acid or base. Effect of ambient temperature was also investigated. Experiments

were run at the temperatures of 10, 20, 30, 40 and 50 °C the conditions designated earlier experiments.

Results

Activation Exponents

Clinoptilolite samples were activated using 1 M HCl or NaOH to increase the adsorption capacity. For this purpose, firstly 1, 2 and 3 ml 1M HCl were added in three conical flask containing 2 grams of clinoptilolite and 100 ml distilled water separately, secondly 1, 2 and 4 ml NaOH were added in an other conical flask containing 2 grams of clinoptilolite separately, and one conical flask containing 2 grams of clinoptilolite was kept without acid or alkali addition. Results shows that the best activation condition was addition of 2.0 ml 1 M HCl in 100 ml distilled water containing 2 grams of clinoptilolite.

Effect of initial Cu(II) concentration by the clinoptilolite adsorption

Determination of effective Pb^{+2} concentrations on removal efficiency of clinoptilolite was studied with addition of 2.0 grams of activated adsorbent in different concentration of Pb^{+2} in 100 ml water solutions. Figure 1 shows that the maximum removal efficiency was obtained with 1.6 mg/L Pb^{+2} concentrations, a little decrease was found below from this values. Later on, decreasing removal efficiency was detected with increasing initial heavy metal concentrations in the solutions. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and that as metal concentrations increase, these sites become saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available: all are occupied (Argun *et. al.*, 2007b).

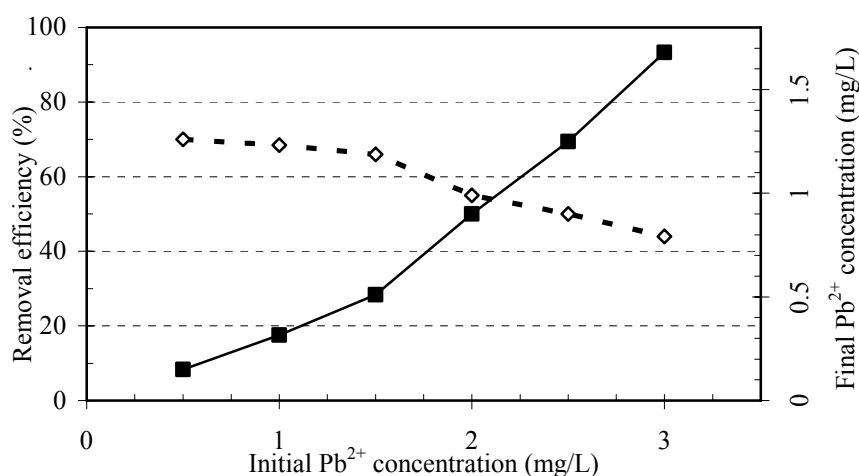


Figure 1. Pb^{+2} removal efficiency of clinoptilolite from aqueous solutions containing different Pb^{+2} levels. Symbols are ■, final Pb concentration (mg/L) in the samples and ◊, removal efficiency (%).

Effect of adsorbent doses on the Pb^{+2} adsorption by the clinoptilolite was investigated with changed adsorbent doses from 1.0 to 4.0g that maximum removal efficiencies have been achieved to be 67% with 2.0 g clinoptilolite/100 ml solution (Figure 2). Residual Pb^{+2} concentration seemed until to 2.0 g a clear increasing and than a smaller increasing after this value.

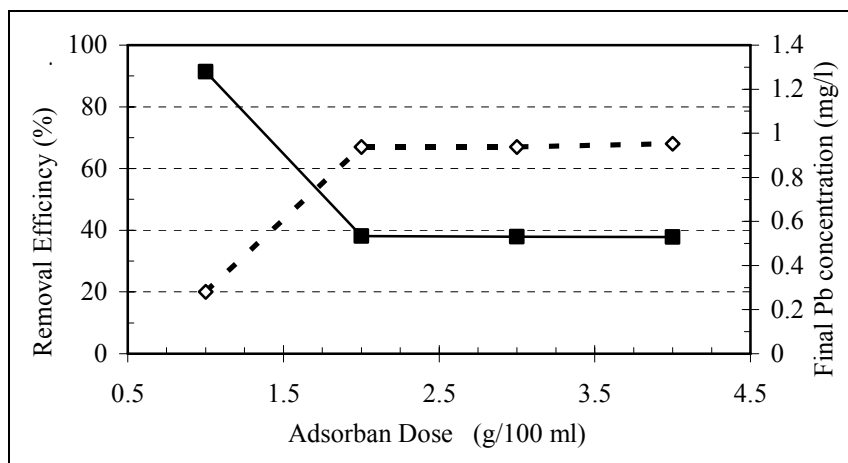


Figure 2 Effect of different adsorbent dose of clinoptilolite for Pb²⁺ adsorption. Symbols are ■, final Pb concentration (mg/L) in the samples and ◇, removal efficiency (%).

Solution pH effect on adsorption capacity

Effect of pH on the adsorption of Pb(II) by the clinoptilolite was also investigated with the changing pH values from 3.0 to 9.0. The results depicting the dependence of the Pb (II) removal as a function of pH shows that maximum removal efficiencies have been achieved to be 86 % at pH 5.0 (Figure 3). According to different pH values Pb ions may present in different forms. For this reason, Pb²⁺ ions dominates at pH<6 and Pb(OH)₂ dominates at pH>5 (Argun *et al.*, 2005).

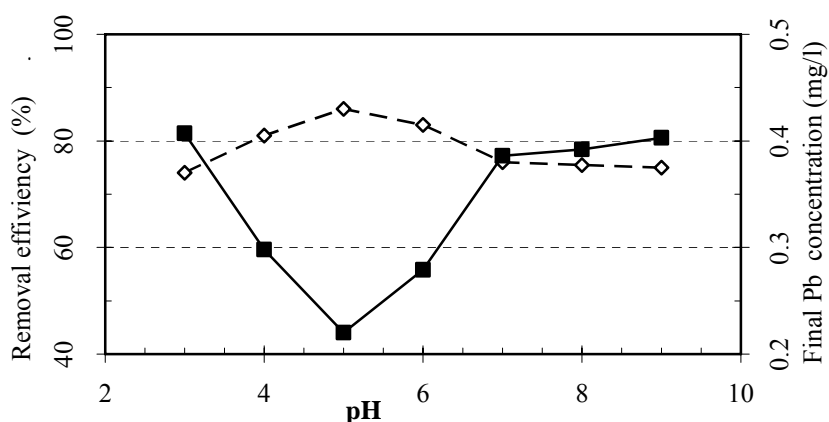


Figure 3. Effect of solution pH on removal efficiency of Cu²⁺ from water. Symbols are ■, final Pb concentration (mg/L) in the samples and ◇, removal efficiency (%).

Effect of sample temperature on Cu²⁺ removal capacity of clinoptilolite

Activated 2 grams of clinoptilolite in 100 ml water at pH 5.0 was tested for adsorption of Pb²⁺ at different sample temperature between 10 to 50°C. Results show that optimum working temperature was about 30 °C (Figure 4). Removal of Pb²⁺ from the water was 88% at this temperature, it was lowered at lower and at higher temperatures

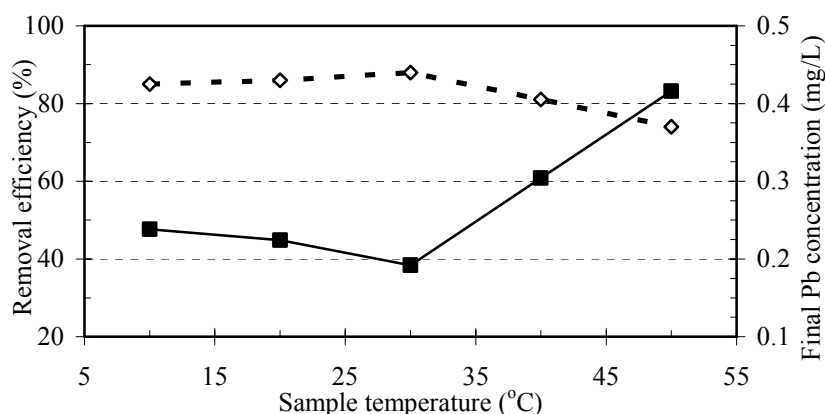


Figure 4. Effect of sample temperature on the clinoptilolite removal efficiency of Pb^{+2} from the water. Symbols are ■, final Pb concentration (mg/L) in the samples and ◇, removal efficiency (%).

The equilibrium adsorption isotherm for lead on activated clinoptilolite was plotted for varying adsorbent dose changing from 0.25 to 3.0 g L⁻¹) and fixed initial lead concentration (1.6 mg L⁻¹) at pH 5.0. The percentage of lead adsorption decreased with increasing adsorbate amount, which indicates that the adsorption depends upon the availability of the binding sites for lead. In order to determine the adsorption capacity of the activated clinoptilolite, the equilibrium data for the adsorption of lead were analyzed in the light of adsorption isotherm models. Mostly used adsorption isotherms are Langmuir and Freundlich equations which were given below respectively (Eqs. 1 & 2):

$$\frac{1}{x/m} = \frac{1}{a} + \frac{1}{ab} \frac{1}{c} \quad (1)$$

$$\ln \frac{x}{m} = \ln k + \frac{1}{n} \ln c \quad (2)$$

where x/m is the amount of lead adsorbed from per unit weight of adsorbent (mg g⁻¹), c is the concentration of lead at equilibrium (mg L⁻¹), $1/ab$ is slope for plot with $1/a$ contact point on y axis for Langmuir adsorption isotherm, and $1/n$ is slope for plot with contact point of $\ln k$ constant on crossing point of y axis for Freundlich adsorption isotherm. The straight line nature of the graph indicates that the adsorption confirms the Langmuir model. The experimental data points were fitted to the Langmuir equation (Figure 5), but it was not fit well to the Freundlich equation.

Chemical kinetics of lead removal was also investigated in batch reactor for 60 min. contact time that checked with 0th, 1st, 2nd and 3rd order reaction equations. Only our data is quite well fit to 2nd order reaction kinetic (Figure 6). Square of correlation coefficient was $R^2=0.9806$ which confirms good relation between contact time and concentration change by experimental period. Reaction kinetic of lead removal from the aqueous environment by clinoptilolite is 2nd order that adsorption of clinoptilolite was physical character and it is suitable for reuse.

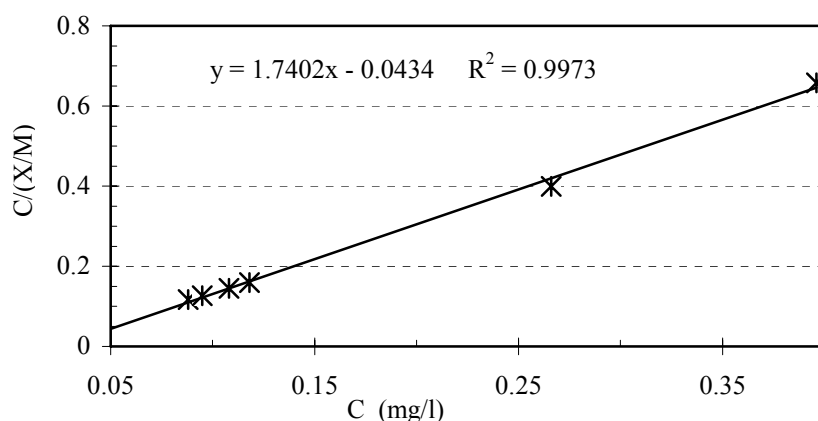


Figure 5. Langmuir adsorption isotherm plot for phosphate adsorption of activated red-mud

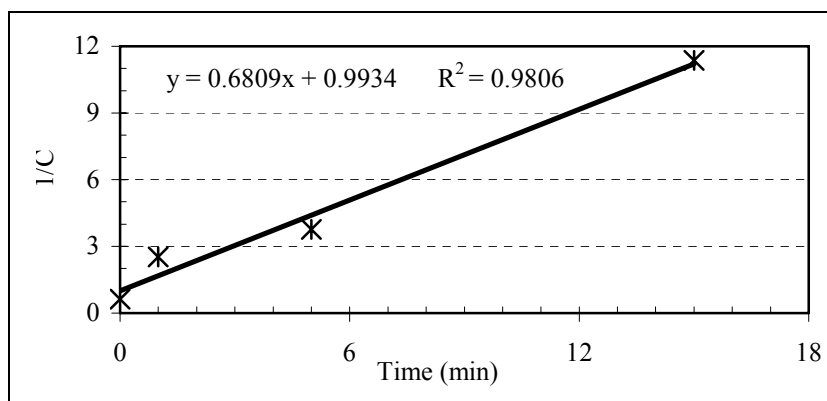


Figure 7. Reaction kinetic (2nd order) plot for the lead adsorption of activated clinoptilolite (1,6 mg L lead concentration and 15 min contact time period).

Discussions

This paper presents the results of Pb(II) ions removal from aqueous solution using a common, naturally occurring clinoptilolite. Operational parameters such as initial Pb(II) concentrations, adsorbent dose, pH of the solution, temperature, and contact time clearly affect the removal efficiency. The optimum Pb(II) removal by the clinoptilolite was obtained at pH 5. At pH higher than 6, lead removal probably resulted primarily from precipitation rather than adsorption.

According to results reported in this study, lead adsorption mechanisms by clinoptilolite may be explained as follows:

1. Vander-walls and hydrogen binding of lead with hydroxyl group of clinoptilolite surfaces.
2. Ion exchange between Pb(II) ions and exchangeable cations (Na, K *etc.*) which balance negative charge of aluminium atoms.
3. Diffusion of Pb(II) through selective sieve of clinoptilolite named as molecular sieve (Mc Bain, 1932).

According to these results, natural clinoptilolite appeared to be a promising adsorbent for the removal of the lead from the polluted water. A process using the clinoptilolite for the removal of heavy metal seemed to be potentially more economical than current process

technology. However, further studies would be suggested, since different metals and different adsorbents are known to have different properties structures.

Heavy metals affect to human health because of their harmful effect. Nevertheless, a lot of heavy metals were using in the industry and they join to food chain. In this respect, wastewaters coming from pollution sources must be treated to decrease their concentration down to limits given in water regulations before to give in the environment. Main principle removal processes base to chemical precipitation of metal ions as -hydroxide or -sulphide. Adsorption, ion exchange, membrane filtration and reverse osmosis *etc.* were used for advanced treatment. Removal of the metal pollution from the water with the classical methods was not enough sufficient, practical and economical. Ion exchange method may be used after pre-treatment operation. Most of the heavy metals recovery was not easy from the precipitate and economic. For this reason, adsorption processes by the natural zeolites may be preferred in the application.

In this investigation, a natural zeolite, clinoptilolite, as an adsorbent was used for removal of lead from the water and very high removal efficiencies were found with different working conditions. Clinoptilolite was activated treating with different concentrations of acid and alkali solution in the first step. Tests in this investigations show that optimum activation condition was addition of 2 ml 1 M HCl in 100 ml water containing 2 grams of clinoptilolite.

After activation process, other experimental conditions were investigated. Second test was determination of usage of concentration of Pb^{+2} which is optimum at $1,6 \text{ mg L}^{-1}$. Removal rate was reached about 66% with this lead concentration. In a separate investigation (Dursun et al. 2007), with activated clinoptilolite at same condition given above and $40 \text{ mg L}^{-1} \text{ Cu}^{+2}$ concentrations adsorption solution was optimum condition.

pH of the adsorption solution was other important condition which was tested. A maximum removal efficiency of %86 was found at pH 5. This showed that clinoptilolite was activated in acidic condition changing cations with H^+ ions and Pb was $+2$ ions form in the working solution. After this experiment temperature and contact time were determined. Removal efficiency was increased until 30°C , and then decreased.

All these experimental results show that clinoptilolite is suitable adsorbent for removal of heavy metals. On the other hand clinoptilolite is available in rest of Turkey and economical price. It is suitable material for heavy metal removal from the industrial waste water.

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