Adsorption of lead from aqueous solutions using Kaolinite.

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Abstract---

In this study, removal of lead (Pb^{2+}) from aqueous solutions is investigated using zeolite. During the removal process, batch technique is used, and the effects of pH, adsorbent amount, and heavy metal concentration and agitation time on adsorption efficiency are studied. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms are applied in order to determine the efficiency of zeolite used as an adsorbent. Results show that freundlich model is linear. It is determined that adsorption of Pb^{2+} is well-fitted by the pseudo second order reaction kinetic. It is concluded that zeolite can be used as an effective adsorbent for removing Pb^{2+} from aqueous solutions.

Index Terms--- Adsorption, Lead, Adsorption efficiency, Reaction kinetics

I.INTRODUCTION

Heavy metals pollution has become one of the most serious environmental problem today heavy metals means metal ion those specific weight is usually more than 4 to 5gl-1.Industrial process like metal plating, fertilizer industry, mining dying in textile produce huge amount of wastewater containing heavy metals daily. Metal like lead , mercury, cadiumium ,nickel , chromium , copper, zinc , cobalt are at elevated concentration detrimental to human health, environment ,ecosystem stability . Threshold values have been set for these heavy metal fo wastewater discharge into natural recipients and drinking water[1-3].

The heavy metals are of toxic characteristics due following facts

A) Non-degradability
B) Can convert in more toxic form from less toxic form in certain environmental condition
C) Bio accumulation can damage normal physiological activity
D) Toxic at very low concentration

Therefore, the heavy metal levels in wastewater, drinking water, and water used for agriculture should be reduced to the maximum permissible concentration [1].

Lead (Pb) is one of the major environmental pollutants because of its presence in automobile fuel and subsequent emission into the atmosphere in the exhaust gases [4,5]. Moreover, it penetrates to the water environment through effluents from lead smelters, battery manufacturers, paper and pulp industries, and ammunition industries [6,7] .
Several methods have been applied over the years on the elimination of these metal ions present in industrial wastewaters and soils. The usual methods for removal of heavy metal ions from aqueous solutions can be ordered as chemical precipitation, ion-exchange, solvent extraction, ,ultrafiltration, reverse osmosis, electrodialysis, and adsorption[8-10] . Adsorption is one of the important procedures for the removal of the heavy metals from the environment. The main properties of the adsorbents are strong affinity and high loading capacity for the removal of heavy metals. Natural adsorbents have generally these properties. Ion-exchange and adsorption mechanisms of clay minerals have been used to remove different heavy metals from aqueous solution [11-14].

Natural zeolite is an abundant resource of aluminosilicate available all over the world. The most important natural zeolite is clinoptilolite. In the past years, natural zeolite has been explored as effective adsorbent for removal of various heavy metals and dyes However, in the previous studies, only single component system was investigated and few investigations on binary system (dye and metal ion) have been reported to consider competitive adsorption. Some investigations on metal ions in multi-component adsorption on natural zeolite have been reported. Understanding of multicomponent interaction with natural zeolite would be very helpful to take full advantage of clinoptilolite properties for tertiary treatment [18].

The objective of the present work is to study the adsorption characteristics of the Pb(II) ion from aqueous solution using zeolite . Well-known isotherm models were applied to the equilibrium data.

NOMENCLATURE

C_e equilibrium concentration of solution
Co initial heavy metal concentration
C_2 integration constant of pseudo-second order reaction kinetic
E main energy of adsorption
K equilibrium constant of Langmuir isotherm
e Polanyi potential
k_2 rate constant of pseudo-second-order adsorption kinetic
K_f Freundlich isotherm constant
K' adsorption energy constant
m adsorbent mass
n adsorption intensity
R gas constant
r^2 correlation coefficients
t time
T temperature
V solution volume
V_m monolayer capacity for Langmuir isotherm

V'_m D-R adsorption capacity
q_e amount of adsorbed heavy metal per unit adsorbent mass
q_t amount of heavy metal adsorbed at time t

INSTRUMENTATION

Lead analyses were carried out titrations method. Sedko water shaker was used in all adsorption experiments and pH adjustments were performed in systronics model pH-meter.

CHEMICALS

Lead Nitrate ($Pb(NO_3)_2$) was used in adsorption experiments. pH adjustments was carried on using 0.1N hydrochloricacid,0.1Nsodiumhydrooxide the chemicals used in lead analyses were supplied from Finar chemicals.

ADSORBENT

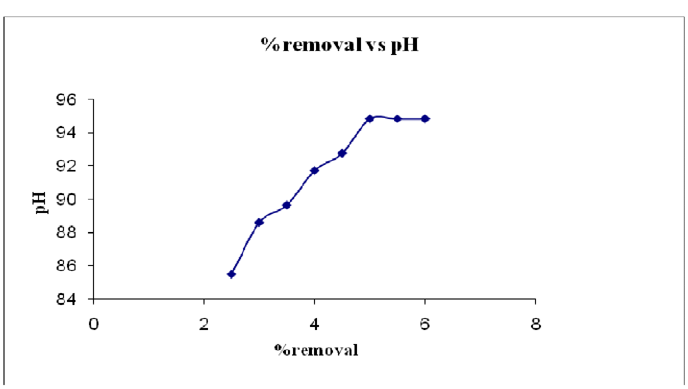
TABLE 1
CHEMICAL COMPOSITIONS OF ZEOLITE

SiO_2	61 - 68 %	by wt
$Al_2 0_3$	15 - 20 %	by wt
Fe_2O_3	2 - 3 %	by wt
MgO	2 - 3 %	by wt
CaO	1 - 3 %	by wt
Na_2O	2 - 3 %	by wt
K_2O	0.05 - 1 %	by wt

ADSORPTION MODELS

Equilibrium isotherms for lead were obtained by performing batch adsorption studies. Solutions of 200 mg/L concentration were adjusted to optimum pH values and adsorbent amounts ranging between 100and800 mg were added to solutions.
The adsorbed heavy metal amount (qe) per unit absorbent mass was calculated as follows.

Where Co is the initial heavy metal concentration, Ce is the concentration of heavy metal at equilibrium (mg/l).m is the clay mass (mg) and V is the solution volume (L).
Calculations were made by using these data and adsorption curves were obtained.



zeolite was used as the adsorbent. The chemical composition of zeolite is provided in Table 1.

METHODOLOGY

Adsorption of lead with zeolite was carried out in a batch reactor. 1000 mg/L of lead stock solution was prepared by dissolving 1.598 g of ($Pb(NO_3)_2$ in 1 L distilled water. Standard lead solutions ranging between 25and 300 mg/L were prepared by diluting the stock solutions. The volume of the sample was determined to be 25ml. Samples with zeolite content in the range of 100-800 mg were taken from the shaker at regular contact time intervals and the zeolite was separated by filtering. The concentration of lead remained in the solution was analyzed by titration method In the study, the effects of several factors such as pH, concentration of solution, zeolite mass and contact time on lead removal efficiency was examined.

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

KINETIC STUDIES

Kinetic studies for lead were performed by using concentrations. Optimum conditions were used during these experiments. pH was adjusted to 5 and zeolite mass was 400 mg for lead.

RESULTS AND DISCUSSION
EFFECT OF PH

In order to investigate the effect of pH on lead adsorption with zeolite, metal solutions of 25 mL in volume and 200 mg/L in concentration was used at pH ranging from 2 to 6. In the experiments, clay content was kept constant (400 mg) and agitation time was determined to be 90min at 100 rpm. The results are shown in Fig. 1.

The highest removal efficiency in the lead adsorption with zeolite obtained at 5. at lower pH values the adsorption efficiency was decreased. The effect of pH changes due to the adsorbent type, its behavior in the solution and the type of ions adsorbed [8]. In this study, the optimum pH values for the lead removal was determined as 5.

Fig.1. Effect of adsorbent dosage on the removal of Pb^{2+} by zeolite. Initial metal concentrations 200 mg/L, dose of adsorbent400 mg, contact time 90 min

Optimum pH value was used in the further experiments analyzing the effects of other factors such as the amount of adsorbent, the metal concentration and the agitation time.

EFFECT OF ADSORBENT DOSAGE

In experimental studies carried on in order to determine the optimum adsorbent dosage, solutions with an initial metal concentration of 200 mg/L was used at optimum pH values. During the contact time of 90 min, the amount of adsorbent added to the solutions varied between 100and 800 mg. The results are shown in Fig. 2.

In the lead removal, it is seen that the adsorption efficiency increases as the adsorbent amount increases. The increase in the efficiency can be explained by the increasing surface area where the adsorption takes place. As seen in Fig. 2, optimum adsorbent dosages that can be used in lead removal is1.6 g/100ml.

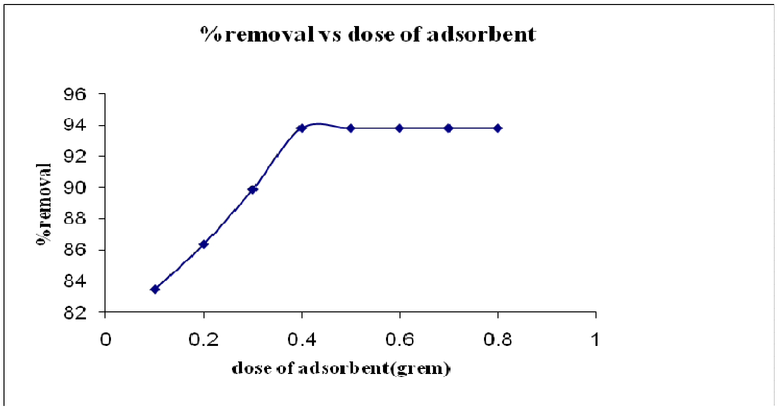


Fig.2. Effect of clay dosage on the removal of Pb^{2+} by zeolite. Initial metal concentrations 200 mg/L, pH 5, contact time 90 min

EFFECT OF METAL CONCENTRATION

An optimum concentration was determined after experimental studies done under various metal concentrations ranging between 25 and 300 mg/L. The adsorption efficiency increased to a certain level, and remained stable as the concentration increased. Following the saturation on the surface where the adsorption takes place, no more metal ions can be adsorbed. The optimum metal concentration was determined as 200 mg/L. The results obtained from the experimental studies are shown in Fig. 3.

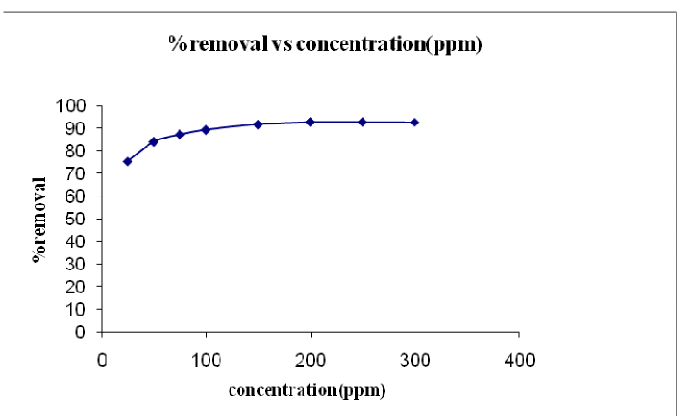


Fig.3. Effect of adsorbent dosage on the removal of Pb2+ by zeolite. Dose of adsorbent 400mg, pH 5, contact time 90 min

FREUNDLICH ISOTHERM

Where K_f is the Freundlich constant (mg/g) and n is the adsorption intensity: The linear form of the Eq. (4) can be written as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

It is seen that the Freundlich isotherm curves are linear zeolite adsorption. The Freundlich constant K_f and adsorption

EFFECT OF AGITATION TIME

The optimum time for lead removal was determined at 15 min, respectively (Fig. 4). As a result of the experimental studies, it is seen that high efficiency for lead adsorption can be obtained at short time periods.

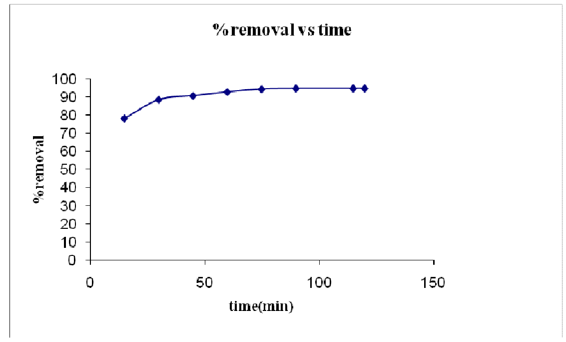


Fig.4. Effect of contact time on the removal of Pb2+ by zeolite. Initial metal concentration 200 mg/L, adsorbent dosage 400 mg, pH 5.

ADSORPTION ISOTHERMS

LANGMUIR ISOTHERM

Langmuir isotherm models the single coating layer on adsorption surface. This model supposes that the adsorption takes place at a specific adsorption surface. The attraction between molecules decreases as getting further from the adsorption surface . Langmuir isotherm can be defined according to the following formulas:

$$q_e = V_m k C_e / 1 + k C_e \quad (2)$$

Where q_e is the amount of adsorbed heavy metal per unit clay mass (mg/g), Vm is the monolayer capacity, k is the equilibrium constant and Ce is the equilibrium concentration of the solution (mg/L).

Eq. (2) can be written in the following linear form:

$$C_e/q_e = 1/kV_m + C_e/V_m \quad (3)$$

$$q_e = K_f C_e^{1/n} \quad (4)$$

Where K_f is the Freundlich constant (mg/g) and n is the adsorption intensity: The linear form of the Eq. (4) can be written as:

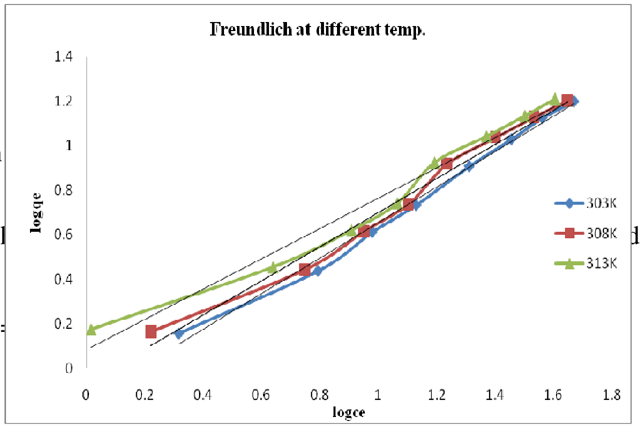
The results obtained from the empirical studies were applied to Langmuir isotherm. The dependence of C_e/q_e from C_e was obtained by using empirical results (Fig. 5a).

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained by following equation.

intensity n for lead are calculated from the slopes of these curves (Table 4).

DUBININ–RADUSHKEVICH (D–R) ISOTHERM

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. D–R isotherm is commonly used to describe the sorption isotherms of single solute systems. In previous



ln

wl d

e =

Where R is the gas constant (kJ K^{-1} mol^{-1}) and T is the temperature (K).

The main energy of adsorption (E) is calculated by using the following formula:

$$E = (-2K)^{-0.5} \quad (8)$$

where E gives information about the physical and chemical features of adsorption.

The D–R isotherm is applied to the data obtained from the empirical studies. A plot of ln q_e against e^2 is given in Fig. 5c.

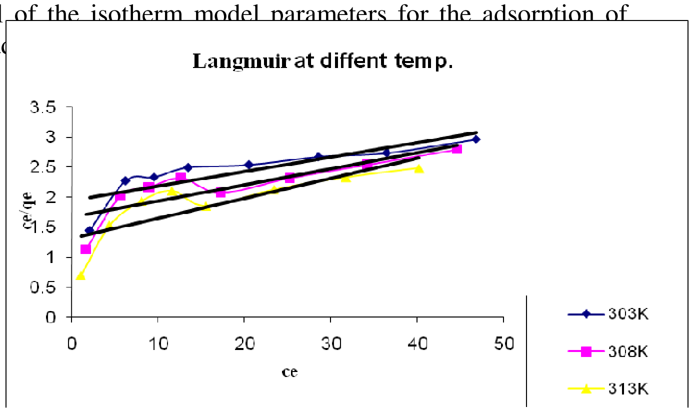
In the D–R isotherm, adsorption capacities (V_m), adsorption energy constants (K) and the main adsorption energies (E) are calculated for lead removal.

All of the isotherm model parameters for the adsorption of lea

(a)

(b)

(c)



studies, D–R isotherm was used to express the adsorption processes of zeolite. The D–R isotherm, apart from being analogue of Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogeneous surface or constant adsorption potential [8].

The D–R isotherm is expressed as:
per unit clay mass, V'm is the D–R adsorption capacity (mg/g), K is the constant related with adsorption energy (mol^2 k/J^2), and e is the Polanyi potential.
According to the Polanyi potential (e) can be given as:

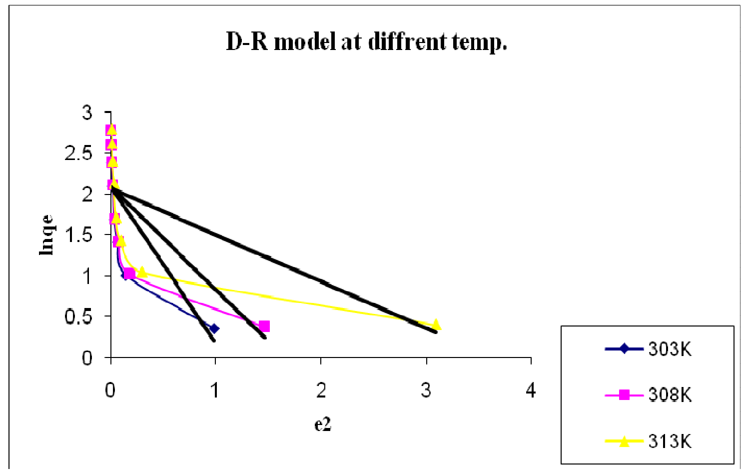


Fig. 5. Langmuir (a), Freundlich (b), and D–R (c) adsorption models for interactions of Pb^{2+} on zeolite.

TABLE 2 VALUES OF LANGMUIR PARAMETERS OF LEAD FOR ZEOLITE AT DIFFERENT TEMPERATURE

Temp(k)	Langmuir parameters		
	v_m	k	R^2
303	41.32	0.02	0.646
308	37.17	0.016	0.74
313	30.21	0.012	0.658

TABLE 3 VALUES OF FREUNDLICH PARAMETERS OF LEAD FOR ZEOLITE AT DIFFERENT TEMPERATURE

Temp(K)	Freundlich parameters		
	n	K_f	r^2
303	1.25	0.711	***0.992***
308	1.305	0.35	***0.984***
313	1.472	1.21	***0.972***

TABLE 4 VALUES OF D-R PARAMETERS OF LEAD FOR ZEOLITE AT DIFFERENT TEMPERATURE

Temp(K)	Dubinin-Radushkevich parameters		
	Vm	E	r^2
303	8.03	0.511	0.602
308		0.88	0.580
313	7.9	0.9351	0.551

KINETICS OF ADSORPTION

Adsorption kinetics are used in order to explain the adsorption mechanism and adsorption characteristics.
The adsorption of Pb^{2+} onto zeolite was investigated in terms of the kinetics of the adsorption mechanism by using two models: (natrajan –kalhaf)first-order, pseudo-second-order models. The plots of log(co/ct)versus *t* for the (natrajan-kalhaf)first-order model were not shown as figure because the coefficients of determination for this model at studied temperatures is low ($R^2 = 0.806$) for the Pb^{2+}. The adsorption of Pb^{2+} onto zeolite does not follow the (natrajan –kalhaf)-first-order model because the coefficients of determination is low.

PSEUDO-SECOND-ORDER REACTION KINETIC

Adsorption data was also evaluated according to the Pseudo-second-order reaction kinetic proposed by Ho and McKay [8]:

$$dqt/qt = k_2 (qe-qt)^2 \quad (9)$$

where k_2 is the second order reaction constant. If Eq. (9) is integrated, the following expression is obtained:

$$1/(q_e-q_t) = k_2 t + C_2 \quad (10)$$

In Eq. (10), C_2 is the integration constant of the second order reaction kinetic. With an algorithmic arrangement, the following statement is formed:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (11)$$

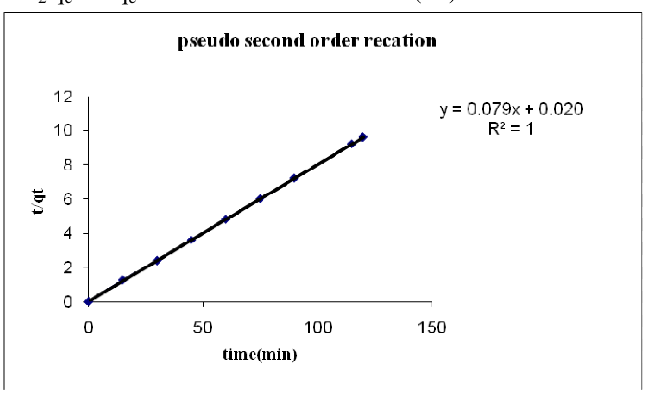


Fig. 6. Pseudo-second order reaction kinetics for the adsorption of lead on zeolite.

The curves in the plot of t/qt against t are linear and k_2 rate constants can be calculated from the slope of these curves (Fig. 6).

CONCLUSIONS

In this study, removal of Pb^{2+} is investigated using zeolite. pH is a significant factor in adsorption processes since it causes electrostatic changes in the solutions. Hydrogen ions themselves are strongly competing with adsorbents. At the end of experiments carried out at 30◦C and 100 rpm, optimum pH values for Pb^{2+} removals are determined as 5.
It is also determined that the adsorption is completed in relatively short time periods. Maximum removal efficiencies were succeeded within 30min metals. Optimum contact times 90 for lead removal.

The empirical values are evaluated according to the Langmuir, Freundlich and D–R isotherms that are generally used to describe the adsorption processes. In the Freundlich isotherm calculated adsorption intensities for lead 1.25,1.305,1.472 respectively. The correlation coefficients for lead are 0.992,0.984and0.972 Moreover, in the D–R isotherm, adsorption energies are calculated to state the physical and chemical characteristics of adsorption. The magnitudes of E for lead adsorption are 0.51,0.88,0.953kJ/mol, respectively. These low values of adsorption energy show that the adsorption has a physical nature.
Pb^{2+} adsorption from aqueous solutions using zeolite with the second order reaction kinetic.

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