

ORIGINAL RESEARCH PAPER

## Removal of Pb(II) by Modified Natural Adsorbent; Thermodynamics and Kinetics Studies

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### ABSTRACT

In the current work, the natural zeolite was modified with cobalt hexacyanoferrate and employed for adsorbent of Pb(II) ions from aqueous solution. The modification was approved by XRD and FTIR techniques. The Pb(II) adsorption capacity enhanced by 1.8 times from 60 mg/g (natural zeolite) to 100 mg/g (modified zeolite) at optimal conditions. Factors such as time, pH, temperature, adsorbent dosage and initial concentration were investigated to optimize the adsorption condition. A fast sorption was observed in the initial contact time and equilibrium was achieved in less than 120 min. The optimum pH for lead removal was between 3 and 6. The adsorption capacity was increased and reached the maximum of 90 % at 2 g/L adsorbent dosage. Also, the adsorption increased as the concentration increased up to 500 mg/L and the sorption became constant at higher concentration. It was found that the double-exponential model describes the lead sorption kinetics and the Langmuir-model describe the isotherms.

**Keywords:** Adsorbent, Cobalt-Hexacyanoferrate, Lead, Modified-Zeolite, Zeolite

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## INTRODUCTION

Water polluted by heavy metals has been considered as a serious problem for their harmful effects on the environment and living organisms, due to their bio-accumulation tendency and persistency in nature. With the rapid development of industries such as battery manufacturing, mining, and smelting factory, wastewaters containing Pb(II) ions are being discharged into the environment water system. Since the compounds of the Leads can accumulate in the body and cause severe saturnine poisoning such as lesions in the central nervous system, brain damage, mental deficiency, anemia, anorexia, vomiting and malaise, the lead is considered as highly toxic to human health [1]. Today one of the serious problems is contamination of surface and

groundwater with heavy metals ions such as Pb(II) ions. So the removal of Pb(II) from wastewater before discharge is important [2]. The techniques such as chemical precipitation, flocculation, electro-flotation, ion exchange, reverse osmosis, evaporation, and adsorption have been used for uptake of Pb(II) from water, [3]. The application of more effective and environmental friendly method is very important for removal of Pb(II) ions. Some of the mentioned techniques have unreliable efficiencies or cause secondary pollution [4]. The adsorption is considered as an effective, selective and easy to perform a method for the removal of Pb(II) ions from the complex mixtures [5-6]. The zeolites as an adsorbent material have advantages, such as facile availability of raw material sources,

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unexpensive and pleasure adsorption ability[1]. They are widely used as adsorbents, ion exchangers, and catalysts which could also be used for drying gases, purification and sewage treatment[1-4]. The structures of natural zeolites include  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra three-dimensional framework. The small aluminum ion is posited in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  produces a negative charge in the zeolite lattice. The net negative charge is balanced by the exchangeable cation ( $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ ). The exchangeable cations can be replaced with heavy metal ions in solutions such as  $\text{Cd(II)}$ ,  $\text{Pb(II)}$ ,  $\text{Zn(II)}$  and  $\text{Mn(II)}$  [7]. Pretreatment and modification of zeolite to cleanse the impurities and alter the properties of zeolite surface through anchoring of new adsorption site would affect the adsorption process of zeolite. Fe-modified zeolites were reported to be capable of adsorbing high concentrations of heavy metals in solutions. The porosity and surface area of the zeolite can be improved with a mineral acid or base modifications [8]. The study showed that the modified of zeolites with  $\text{Al}_2(\text{SO}_4)_3$  increased two times the manganese adsorption capacity of natural zeolites [9]. The highest manganese adsorption capacity is observed in the iron-loaded clinoptilolite [10]. The modification of zeolite with Hexadecyltrimethylammonium surfactant leads to improvement of chromate ions selectivity of product. Metal Hexacyanoferrate ion-exchangers have been widely studied for the recovery of  $\text{Cs(I)}$ ; however, a numerous literature is also citing the possibility to use these materials for the sorption of heavy metal ions. Synergistic effects of zeolite and Metal Hexacyanoferrate improve selectivity and adsorption capacity towards metal ions [11]. However, to our best knowledge, no report of the application of modified natural zeolite with cobalt ferrocyanide for removal lead ions has been published in the scientific literature.

The aim of the current work was to the treatment of natural zeolite as an adsorbent for  $\text{Pb(II)}$  removal from aqueous solution. The effects of solution pH, contact time, initial  $\text{Pb(II)}$  concentration, and adsorbent dosage were investigated.

## EXPERIMENTAL

### Materials, Characterization, and Modification

All chemicals used in this study including of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{K}_3\text{Fe(CN)}_6$ , and  $\text{Pb(NO}_3)_2$  were analytical grade from Merck Co. The  $\text{Pb(II)}$  stock

solutions were prepared by dissolving the lead nitrate salts in deionized water. X-ray diffraction patterns of the natural and modified zeolites were recorded by means of an STOE XD-3A X-ray diffractometer (Cu  $\text{K}\alpha$  radiation,  $k = 0.154 \text{ nm}$ , 40 kV and 30 mA). The Infrared spectra of the natural and modified zeolites were recorded by means of a BOMEM MB-series FTIR spectrometer within the wave number range of  $250$  to  $4000 \text{ cm}^{-1}$  after pelleting with KBr. The modification of natural zeolite was performed according to our previous work [11]. 5 g of the dried and powdered zeolite was added to a 100 ml solution of  $0.1\text{M Co(NO}_3)_2$  at  $25^\circ\text{C}$  for 2 hours. Then the zeolite was washed and mixed with a 100 ml of  $0.1\text{M K}_4\text{Fe(CN)}_6$  solution to deposition of the  $\text{CoHCF}$  in the surface and channels of zeolite. Then the treated zeolite was washed and dried at  $60^\circ\text{C}$  for 2 hours.

### Pb(II) Sorption

The batch adsorption experiments were performed according to the following: a determined amount of the adsorbent (0.1g) was added to 20 ml of  $\text{Pb(II)}$  solutions. The mixture was stirred for a period of time. Then the samples were filtered and the remained  $\text{Pb(II)}$  ions in the solution were determined by ICP techniques. The  $\text{Pb(II)}$  removal capacity was defined as:

$$q_e = (C_i - C_e) \frac{V}{W} \quad (1)$$

Where  $v(\text{L})$  is the volume of  $\text{Pb(II)}$  solution,  $C_i$  (mg/L) is initial  $\text{Pb(II)}$  concentration,  $C_e$  (mg/L) is final  $\text{Pb(II)}$  concentration, and  $w(\text{g})$  is the mass of the solid phase.

The effect of contact time, initial concentration, pH, adsorbent dosage and temperature parameters were studied to determine the modified zeolite properties and the adsorption parameters.

## RESULTS AND DISCUSSION

### Characterization

The XRD patterns of the natural and modified zeolites are shown in Fig. 1. The characteristic reflection peaks at  $2\theta = 10^\circ, 11.3^\circ, 13.2^\circ, 22.5^\circ, 27^\circ, 30.02^\circ$  and  $32^\circ$ , respectively ( belong to clinoptilolite) can be seen in the two samples [12]. In modified zeolite in addition to the clinoptilolite peaks, the characteristic peaks at  $2\theta = 40^\circ, 50^\circ$ , and  $55^\circ$  correspond to (420), (422) and (440) plane of the crystal structure of cobalt hexacyanoferrate also can be seen in pattern (JCPDS card no: 46-907)

[11] which it confirms successful modification of zeolite.

The FT-IR spectra of the natural and modified zeolites are shown in Fig. 1(inset). A sharp peak which appeared at  $2090\text{ cm}^{-1}$ , in the modified zeolite is a characteristic of the cyanide group ( $\text{C}\equiv\text{N}$ ) and confirms the successful modification of the natural zeolite [13, 14].

#### Adsorption: Ph, Adsorbent Dosage, And Temperature Effect

At first the adsorption capacity of non-modified zeolite and modified zeolite were measured and results indicated that the adsorption capacity were 60 and 100 mg/g for non-modified zeolite and modified zeolite respectively (temperature = 298 K, adsorbent dosage= 0.1 g, initial Pb(II) concentration = 500 mg/g, pH = 3-4 and contact time =240 min ). In the adsorption process, the solution pH plays a key role, because  $\text{H}^+$  are strong competing adsorbates and influences on metal ion form, the surface charge of adsorbent, and stability of adsorbent in solution. Fig. 2a shows the influence of pH on the uptake of Pb(II) by modified zeolite. It was seen that the adsorption dependent on solution pH and the removal of metal ion was high when  $2 < \text{pH} < 6$ . In acidic solution, pH  $< 2$  the competition between  $\text{H}^+$  and metal ions for active sites of adsorbent led to little adsorption of Pb(II). In other words in acidic solution higher

concentration and higher mobility of  $\text{H}^+$  led to the preferential uptake of  $\text{H}^+$  ions compared to Pb(II) ions. In alkaline solution,  $6 < \text{pH}$  the precipitation of  $\text{Pb}(\text{OH})_2$  and dissolution of adsorbent decrease the uptake value. The influence of modified zeolite dosage on Pb(II) adsorption was studied in 0.5- 6 g/L dosage ( Fig. 2b). The adsorption capacity was increased with the increase of adsorbent value and reached the maximum of 90 % at 2 g/L adsorbent dosage. Then the increase in dosage caused a slight effect upon ion adsorption. The improvement of adsorption with increasing adsorbent dosage can be attributed to the increase of surface area and available adsorption sites [15]. Slight change of adsorption capacity with more increasing of adsorbent dosage can be attributed to overlapping of the adsorption sites as a result of overcrowding of adsorbent particles. Also at the high adsorbent dosage, the screening effect led to shielding the binding sites of adsorbent from metal ions.

Two main removal mechanisms of Pb(II) by adsorbent are physical adsorption (by negative lattice charge) and ion exchange by cobalt ferrocyanide ( $\text{K}^+$  by  $\text{Pb}^{2+}$ ) and cations of zeolite[11]. The cobalt ions didn't contribute in ion exchange. In fact, the high surface area of zeolite and high adsorption affinity of cobalt ferrocyanide lead to synergistic effects of zeolite and metal Hexacyanoferrate and improve selectivity and adsorption capacity towards metal ions[11].

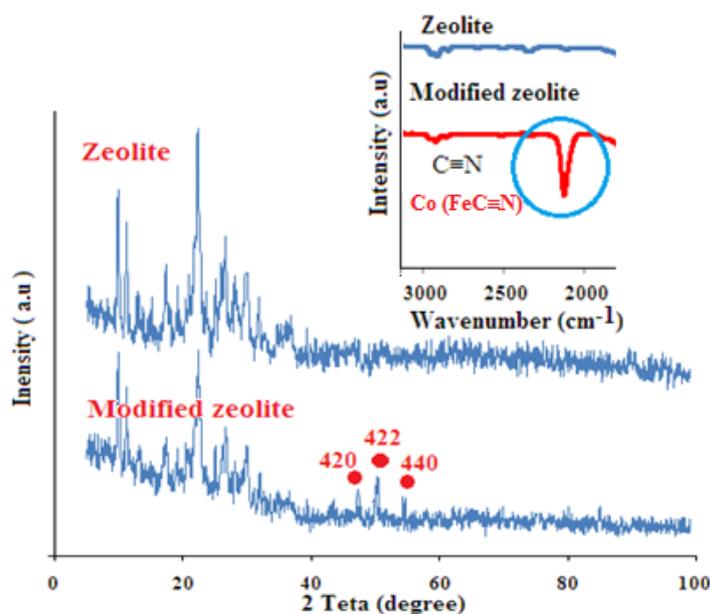


Fig. 1. XRD pattern of natural and modified zeolites (inset: FTIR spectra)

The effect of temperature on the adsorption of Pb(II) on the modified zeolite was investigated at 298, 313 and 333 K (Fig. 2c, d. Table 1). Temperature change results in changes related to both kinetics and equilibrium of adsorption process. Change in the mass transfer resistance, the thickness of the boundary layer surrounding the adsorbent, surface activity of the adsorbent and kinetic energy of the metal ions are the results of temperature change in the adsorption process. As shown, by the increase of the temperature the adsorption capacity was decreased which indicating that the process was endothermic.

The change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of Pb(II) adsorption were determined from the following equation:

$$\Delta G^\circ = -RT \ln K_c \quad (2)$$

Where T(K) is temperature, R is gas constant, and  $K_c$  is the equilibrium constant. The  $K_c$  was

determined from the following equation:

$$K_c = C_e / C_s \quad (3)$$

Where  $C_e$  and  $C_s$  is the equilibrium concentration of Pb(II) on adsorbent (mg/L) and in the solution (mg/L).

The negative value of  $\Delta H$  indicating the exothermic nature of Pb(II) adsorption on the modified zeolite. The negative value of  $\Delta S$  reflects an ordered arrangement of ions around adsorbent particles (at solid/liquid interface) and the negative  $\Delta G$  indicate the spontaneous nature of the process.

#### Time Effect

The rate of adsorption is one of the important criteria for the efficiency of adsorbent and also the mechanism of adsorption can be concluded from kinetic studies. Therefore the study of adsorption kinetics is vital in the adsorption process. So for optimize of experimental condition and determine

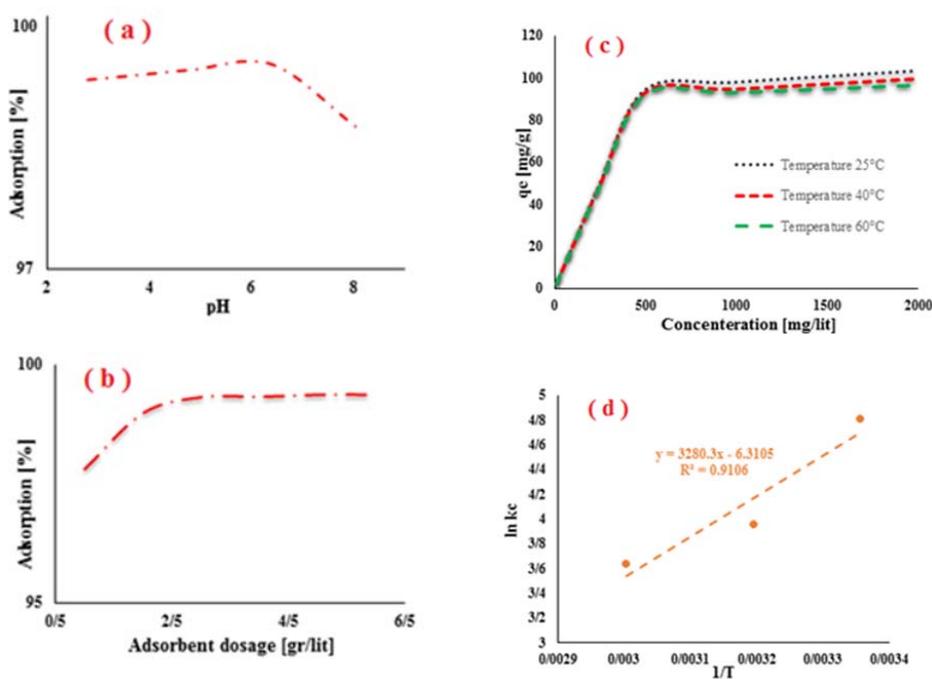


Fig. 2. a) effect of pH, b) effect of adsorbent dosage, and c, d) effect of temperature on Pb(II) adsorption by treated zeolite

Table1. Thermodynamic parameters of Pb(II) on treated zeolite

Metal	E (kJ/mol)			$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol. K)	$\Delta G^\circ$ (kJ/mol)		
	298 K	313 K	333 K			298 K	313 K	333 K
Pb (II)	7.559	7.954	7.319	-27.272	-52.465	-11.638	-10.851	-9.801

of kinetic parameters, the sorption capacity was measured at different interval contact times (15-480 min, at 298°C). The result indicated that in the initial contact time equilibrium was achieved (in less than 120 min). At initial contact step, the large concentration gradient between the solution and adsorbent surface lead to increasing of adsorption rate [16]. Then, the adsorption rate is diminished, because more sorption sites were occupied [17].

The pseudo-first-order, pseudo-second-order, double-exponential, Elovich, and intraparticle diffusion models were used for the fitting of the experimental data (Fig. 3, Table 2).

The pseudo-first-order rate as earliest and common model for describing the adsorption rate is expressed as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

Table 2. Kinetic parameters of Pb(II) sorption on modified zeolite

Kinetic models		
The pseudo-first-order model	$k_1(\text{min}^{-1})$	0.5016
	$q_e(\text{mg/g})$	19.78
	$R^2$	0.5238
The pseudo-second-order model	$k_2'(\text{g/mg min})$	0.5123
	$q_e(\text{mg/g})$	19.82
	$h(\text{mg/g min})$	201.248
	$R^2$	0.8859
Double Exponential model	$D_1(\text{mg/L})$	1.307
	$D_2(\text{mg/L})$	0.8866
	$K_{D1}(\text{min}^{-1})$	0.00761
	$K_{D2}(\text{min}^{-1})$	1.019
	$q_e(\text{mg/g})$	19.89
	$R^2$	0.9864
Intraparticle diffusion model	$k_{id}(\text{mg/g min}^{-0.5})$	0.01291
	Intercept (C)	19.62
	$R^2$	0.8099
Elovich model	$\alpha(\text{mg/g min})$	0.064
	$\beta(\text{mg/g})$	19.48
	$R^2$	0.9212

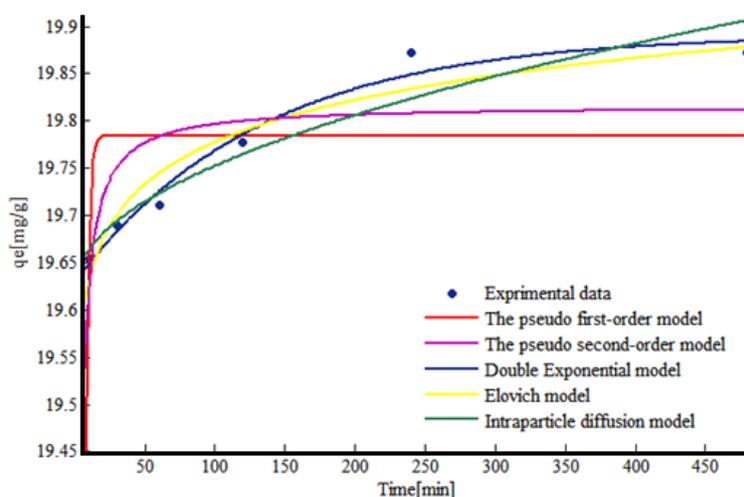


Fig. 3. kinetic models plots for the sorption of Pb(II) from aqueous solutions onto modified zeolite.

where  $q_e$  and  $q_t$  are the amounts of the ions adsorbed ( $\text{mg}\cdot\text{g}^{-1}$ ) on the modified zeolite in equilibrium and at time  $t$ , respectively, and  $K_1$  ( $\text{min}^{-1}$ ) is the rate of the constant adsorption [11].

The pseudo-second-order rate model is expressed as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_t} + k_2 t$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where  $k_2$  is the rate constant of the pseudo-second-order equation ( $\text{g}/\text{mg min}$ ) [9-11].

when the initial adsorption rate  $h$  ( $\text{mg L}^{-1} \text{h}$ ) is:

The mathematical equation of intraparticle diffusion kinetic model is as:

$$q_t = k_{ad} t^{1/2} + c$$

Where  $k_{ad}$  is the rate constant of intraparticle transport ( $\text{mg}/\text{g min}^{1/2}$ ), and  $c$  is the boundary layer diffusion [9-11].

The Elovich equation which describes the adsorption rate on the adsorbent decreases exponentially with an increase in the amount of the adsorbed material as:

$$dq/dt = ae^{-\alpha q}$$

Where  $q$  represents the number of ions adsorbed at time  $t$ ,  $a$  a desorption constant, and  $\alpha$  the initial adsorption rate [9-11].

Chemical reaction and diffusion steps determine the total rate of the adsorption process. Diffusion could have steps such as transfer in solution or in solid. The correlation coefficients were used for the evaluation of the compatibility of experimental data with models. The  $R^2$  of the double-exponential model is the highest value compared with other models. So the double-exponential model can describe the data better than other models. In the double-exponential model, the adsorption of ions by adsorbent occurs in two steps. A rapid first step involving external and internal diffusions, followed by a slow step involving the intraparticle diffusion. The double-exponential model is expressed by the following Equation [18, 19]:

$$q_t = q_e - (D_1/m_{ads}) \exp(-K_{D1}t) - (D_2/m_{ads}) \exp(-K_{D2}t) \quad (4)$$

where  $D_1$  has rapidly adsorbed fractions of ion ( $\text{mg}/\text{l}$ ),  $D_2$  is the amounts of slowly adsorbed fractions of ion ( $\text{mg}/\text{l}$ ), and  $K_{D1}$  and  $K_{D2}$  are rapid and slow rate constants ( $\text{min}^{-1}$ ) respectively. The model parameters of the slow and rapid steps extracted from the experimental data are presented in Table 2.

#### Isotherms

The effect of initial concentration on the adsorption capacity was studied by changing Pb(II) initial concentrations at the range of 10–1500  $\text{mg}/\text{L}$ . The results indicated that the adsorption increased as the concentration increased up to 500  $\text{mg}/\text{L}$  and the sorption became constant at higher concentration. The obtained data were fitted with The Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin isotherm models (Fig. 4). The extracted isotherm parameters, the correlation coefficients ( $R^2$ ) are listed in Table 3. The correlation coefficients ( $R^2$ ) of isotherm equations for Pb(II) was much closer to unity for the Langmuir model than another model. The nonlinear form of Langmuir isotherm can be expressed as [11-17]:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (5)$$

Where  $q_e$  ( $\text{mg}/\text{g}$ ) is the amount adsorbed per unit mass of adsorbent at equilibrium concentration;  $C_e$  ( $\text{mg}/\text{L}$ ) is the equilibrium concentration of the adsorbate;  $q_{max}$  ( $\text{mg}/\text{g}$ ) is the maximum adsorption capacity;  $b$  is the adsorption equilibrium constant, characteristic of the affinity between the adsorbent and adsorbate [11-17].

The non-ideal and reversible adsorption in multilayer would be described by Freundlich isotherm, and the linear form of the equation is:

$$\ln(q_e) = \ln(K_F) + \left(\frac{1}{n}\right) \ln(C_e)$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of ions,  $q_e$  ( $\text{mg g}^{-1}$ ) the amount of adsorbed ions,  $n$  and  $K_F$  ( $\text{mg}/\text{g}$ ) are Freundlich constants related to the intensity of the adsorption and the sorption capacity respectively [11]. In the Temkin isotherm, the interactions between the sorbed species are considered and enthalpy of all the adsorbed molecules in solution is accomplished. The Temkin isotherm is as follows:

$$q_e = B \ln A_T + B \ln C_e$$

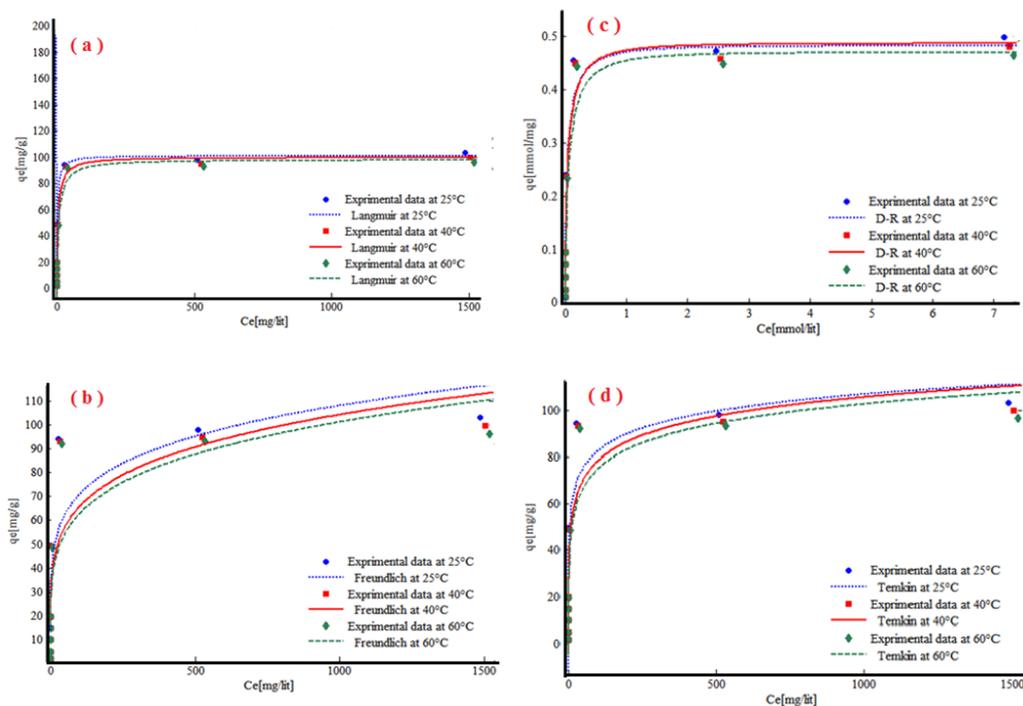


Fig. 4. the sorption isotherms of (a-d) Pb(II), at different temperatures on the modified zeolite.

Table 3. The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) constants and correlation coefficients of isotherm models at different temperature

Isotherms		298 K	313 K	333 K
Freundlich (Pb)	$K_F$ (mg/g)	30.6	26.17	24.11
	$n$	0.1828	0.2002	0.2078
	$R^2$	0.8252	0.8016	0.7959
Langmuir (Pb)	$q_m$ (mg/g)	101.3	100.2	98.35
	$K_L$ (L/mg)	0.436	0.1996	0.1359
	$R^2$	0.9977	0.9954	0.9921
D-R (Pb)	$q_{max}$ (mmol/g)	0.4832	0.4876	0.4709
	$B_{DR}$ (mol <sup>2</sup> /J <sup>2</sup> )	8.75E-09	8.67E-09	9.33E-09
	$E_a$ (kJ/mol)	7.559	7.594	7.319
	$R^2$	0.9594	0.9807	0.9802
Temkin (Pb)	$b_T$ (J/mol)	236	220	230.2
	$K_T$ (L/mg)	26.2	7.51	5.068
	$R^2$	0.9131	0.9157	0.9118

Where  $B$  (J/mol) and  $A_T$  (L/g) are the constants related to the sorption heat and Temkin isotherm equilibrium binding respectively[11]. From the slope and intercept of the  $q_e$  vs.  $\ln C_e$  curve, the constants could be determined.

The Dubinin-Radushkevich (D-R) isotherm is as the following:

$$\ln q_e = \ln q_m - B_{DR} \xi^2$$

Where,  $q_m$  is the maximum of adsorbed ion by adsorbent (mmol/kg),  $B_{DR}$  is a constant related to the sorption energy (mol<sup>2</sup>/kJ<sup>2</sup>); and  $\varepsilon$  is the Polanyi potential ( $RT \ln(1 + 1/C_e)$ ), where  $R$  and  $T$  are the gas constant (kJ/mol.K), the absolute temperature respectively. The  $\varepsilon$  is equal to:

$$\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right]$$

Where  $C_e$  is the adsorbate equilibrium concentration (mg/lit) [11].

## CONCLUSION

The cobalt ferrocyanide modified zeolite was applied for removal of Pb(II) from aqueous media. The Pb(II) adsorption capacity was increased from 60 to 100 mg/g by modification of natural zeolite. The equilibrium was achieved in less than 120 min. The optimum pH was between 3 and 6. The adsorption capacity was increased and reached the maximum of 90 % at 2 g/L adsorbent dosage. The adsorption increased as the concentration increased up to 500 mg/L and the sorption.

## CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest.

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