



A comparative study of Cu(II) and Pb(II) adsorption by Iranian bentonite (Birjand area) in aqueous solutions

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ABSTRACT

Heavy metals such as Cu(II) and Pb(II) are among the hazardous pollutants that lead to severe ecological problems and have a toxic effect on living organisms. The removal of Cu(II) and Pb(II) in the Iranian bentonite experiment were conducted in single component and multi component systems. The bentonite from the Birjand area was characterized by X-ray diffraction pattern and FTIR spectroscopy. The effects of initial Cu(II) and Pb(II) concentration were investigated on the adsorption process. An equilibrium study was performed and followed by five different isotherm models which included two-parameter (Langmuir, Freundlich, Temkin and D-R) and three-parameter (Khan) models. From the Langmuir isotherm, the equilibrium adsorption capacity for Cu(II) is 21.10 to 22.17 mg/g in single component and multi component systems, respectively; and that of Pb(II) is 57.803 to 40.49 mg/g in single component and multi component systems, respectively. The comparative adsorption of Cu(II) and Pb(II) onto bentonite showed that the affinity for Pb(II) to interact with bentonite is higher than Cu(II). Based on the value of the free energy of adsorption for Cu(II) and Pb(II), the interaction between these ions and Iranian bentonite is a chemical adsorption, that is to say, an ion exchange.

1. Introduction

The undesirable trend of hazardous pollutants such as heavy metals in the environment, which leads to severe toxic effects in living organisms and ecological problems, has gained significant global attention [1, 2]. Copper and lead are spread to the environment by natural and industrial activities. Although high concentrations of Cu(II) produces harmful effects, it is an essential nutrient needed by the body in trace amounts. In contrast, Pb(II) is void of any nutritional value and provides no essential function for the human body. High levels of copper also results in health problems such as kidney and liver damage, gastrointestinal disturbance, and disruption of the nervous system [3, 4]. Accordingly, to alleviate the negative health effects of Cu(II) and Pb(II), it is necessary to remove these metals from the wastewater.

In order to prevent the contamination of subsoil, groundwater, and surface water by these elements, a growing interest in the development of materials capable of adsorbing to heavy metals [1] has evolved. Different adsorbents such as red muds and fly ashes [5], waste and natural indigenous materials [6], calcite [7], natural carbonaceous materials [8], and chitosan immobilized on bentonite [3] have already been used for the removal of copper, lead, or both from aqueous solutions. Based on current research, bentonite is one of the significant adsorbents that remove and separate lead and copper from solutions because of its high cation exchange capacity (90–120 meq g⁻¹), high elasticity and plasticity, low cost, easy handling, high abundance as an adsorbent, and easy refining [9,10]. Bentonite is a volcanic clay with montmorillonite as its main clay mineral constituent and belongs to the Smectitic clay minerals with a (Na, Ca)_{0.33}(Al,

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$\text{Mg}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ formula [11, 12]. Montmorillonite has a layer structure with one octahedral coordinated layer of aluminum as the basic structural unit, which is sandwiched between two tetrahedral coordinated layers of silicon. The electrostatic interaction between these layers is a weak Van Der Waals force, which facilitates the intercalation process. The net negative surface charge on the bentonite originates from the substitution of an aluminum ion for a silicon ion and magnesium or iron ions for an aluminum ion in the tetrahedral and octahedral sheets, respectively. The exchangeable cations such as H^+ , Na^+ , and Ca^{2+} on the surface layer are counterbalance charges of bentonite [4, 12, 13]. Since the suitability of Iranian bentonite (Birjand area) for Cu(II) and Pb(II) simultaneous adsorption has not been characterized as of yet, this study was conducted to investigate its effectiveness and evaluate the key factors involved in the adsorption process in the individual and simultaneous adsorption of these ions.

2. Material and Methods

2.1. Materials and physical instrument

A representative sample of bentonite from the Birjand area in southeastern Iran was used without any chemical pretreatment. The sample was ground and sieved by ASTM standard sieves to obtain a particle size of $-150 \mu\text{m}$ in diameter. All chemical compounds were purchased from the Merck Company and used without further purification. The copper and lead solution was prepared by dissolving $\text{Cu}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ in deionized water. The Pb(II) and Cu(II) concentration after adsorption was determined using a Unicom 939 atomic absorption spectrometer (AAS). The XRD pattern and XRF were obtained by a Philips X-ray diffract meter 1,140 ($\lambda = 1.54 \text{ \AA}$, 40 kV, 30 mA, calibrated with Si-standard) and a Philips X-ray diffract meter Xunique II (80 kV, 40 mA, calibrated with Si-standard), respectively. The Fourier transform infrared (FTIR) spectra was recorded on a Shimadzu IR instrument from 4,000 to 400 cm^{-1} by using KBr pellets.

The adsorption percentage and results based on mg/g were calculated by the following equations:

$$\alpha = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = C_0 - C_e \times \frac{V}{m} \quad (2)$$

where α is adsorption percentage, $C_0(\text{mg/L})$ is the initial concentration, $C_e(\text{mg/L})$ is the concentration in the solution after the adsorption process, $q_e(\text{mg g}^{-1})$ is the amount of adsorption, $V(\text{L})$ is the volume of the solution, and $m(\text{g})$ is the mass of bentonite.

2.2. Experimental method

The lead and copper adsorption experiments were carried out by using batch equilibrium. All the adsorption

experiments were conducted in a 250mL glass reactor using a magnetic stirrer bar at ambient temperature. In this study, the influence of lead and copper initial concentration (from 100 to 1250 mg/L) on total adsorption was investigated in the condition of 1.5 g bentonite with a particle size of $-150 \mu\text{m}$ at 298 K with the stirring rate of 600 rpm during a contact time of 30 min. To investigate adsorption isotherms models (Langmuir, Freundlich, Temkin, Dubinin–Radushkevich and Khan), a weighted amount of bentonite (1 g) was added to 100mL of lead solution with different concentrations ranging from 100 to 1250 mg L^{-1} . These experiments were conducted in two part, in the individual solution of Cu(II) or Pb(II) and in the solution which contained both of Cu(II) and Pb(II) ions with the same initial concentration.

After each test, the solution was filtered off and the concentration of the remaining metal ions in the solution was determined by atomic absorption spectrometry.

2.3. Equilibrium studies

The capacity of a sorbent to adsorb a specific metal ion and relations between adsorbent and adsorbate in equilibrium are usually characterized by isotherm models. Isotherm models have an important role in the identification of an adsorption process and the design of an adsorption system. To achieve this goal, five different isotherm models which include two (Langmuir, Freundlich, Temkin and D-R) and three-parameter (Khan) models were used for analysis of the equilibrium adsorption of copper and lead ions onto the bentonite. All the models were analyzed in individual and simultaneous adsorption of Cu(II) and Pb(II). The equations of these models are represented in Table 1. The two-parameter models were fitted by the linear form of the equations and their parameters were calculated by linear regression; further, non-linear regression MATLAB software was employed for determination of the constant value in the three-parameter models.

In addition to the correlation coefficient (r^2), the data of the adsorption evaluation set to confirm the best fit of isotherm models, the Standard deviation (S.D.) was also calculated according to following equation:

$$S.D = \sqrt{\frac{\sum [(q_{e,exp} - q_{e,cal})/q_{e,exp}]^2}{(n - 1)}} \quad (3)$$

Where $q_{e,exp}$ is the experimental data of adsorption and $q_{e,cal}$ is the calculated data from the adsorption models and number of experimental data. If the obtained data from the model were similar to the experimental data, the S.D will be a small number near to zero; if the S.D tends towards 1, it shows that the obtained data were not fit to the selected model.

3. Result and Discussion

3.1. Characterization of the Bentonite

X-ray diffraction (XRD) is an essential tool in the identification and characterization of bentonite. Fig.1 shows the XRD pattern of bentonite. It reveals that the constituents of this sample are quartz, oligoclase, gypsum, montmorillonite, and illite. The diffractions at 8.93°, 19.89°, and 26.69° (2θ) correspond to the (001), (002), and (003) planes overlapped with the illite diffraction peak. The bentonite samples contained a modest amount of illite impurity. In addition, the main impurity in this sample was quartz, which is observed in the XRD pattern with the main diffraction peak at 27.73° (2θ) [11, 14]. Infrared spectroscopy is usually used to identify solid-state structures and functional groups of clay. The presence of two bands at 3,627, and 3,432 cm⁻¹ indicate the stretching vibration of the O–H bond (Fig. 2). The band at 3,627 cm⁻¹ is due to the hydroxyl linkage of the bentonite structure and the broad band at 3,432 cm⁻¹ is due to the presence of the water molecule in the structure [15]. The bending vibration band of H–O–H for the water molecules is observed at 1,635 cm⁻¹. The strong and broad band at 1,040 cm⁻¹ can be attributed to the Si–O stretching vibration of the Si–O–Si linkage of the tetrahedral sheets in the montmorillonite structure [16]. The two bands at 467 and 519 cm⁻¹ represent the bending vibration of the Si–O–Al and Si–O–Si bonds, respectively. The vibration band at 693 cm⁻¹ and its small shoulder (with a lower intensity, which is not assigned in Fig. 2) can be related to the deformation and bending modes of the Si–O–Si bond. The presence of quartz in this sample is indicated by a shoulder at 796–777 cm⁻¹ [11, 17, 18].

3.2. Effect of Cu and Pb initial concentration

For set conditions of bentonite to a liquid ratio (m/V= 15 g/L) and the particle size of ~150 μm, the adsorption of lead and copper ions onto the bentonite has been studied for different initial concentrations ranging from 100 to 1250 mg L⁻¹. The results are shown in Fig. 3. The removal percentage of metal ions was decreased by increasing the initial concentration from 100 to 1250 mg L⁻¹. This shows that the Cu (II) and Pb(II) uptake was limited to the active adsorption sites of bentonite

3.3. Effect of Cu and Pb initial concentration

In order to investigate equilibrium isotherm models in this study, five different models which include two (Langmuir, Freundlich, Temkin and D-R) or three-parameter models (Khan) were examined. The equations of the models and their parameters value were represented in Table.1 and 2, respectively.

3.4. Equilibrium studies of individual Cu and Pb adsorption onto bentonite

In order to investigate equilibrium isotherm models in this study, five different models which include two (Langmuir, Freundlich, Temkin and D-R) or three-parameter models (Khan) were examined. The equations of the models and their parameters value were represented in Table 1 and 2, respectively.

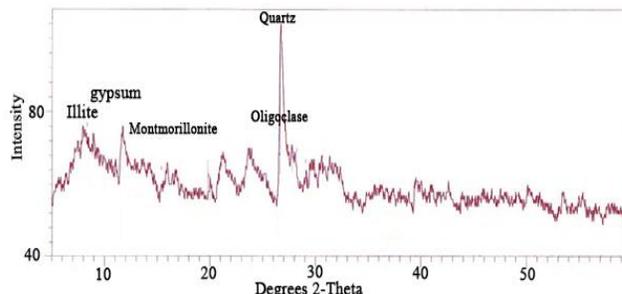


Fig. 1. XRD pattern of bentonite.

• Langmuir isotherm model

The linear form of the Langmuir isotherm model, presented in Table 1, is assuming that the adsorption of metal ions is homogeneous (uniform) onto the surface with a finite number of adsorption sites and identical energy. In Langmuir's equation, K_L is a constant that is related to the binding energy of the active site of the adsorbent. The value of the adsorption coefficients K_L that are related to the apparent energy of sorption for Pb(II), was greater than Cu(II) which indicates that the Pb(II) ions and bentonite are more significantly interacted (Table 2). The maximum adsorption capacity is calculated from the slope of C_e/q_e vs. C_e (Table 1). The maximum adsorption capacity of Pb(II) and Cu(II) are 57.8 and 21.097 mg/g, respectively, with a correlation coefficient (r^2) greater than 0.94. These values of adsorption capacity showed that the energy of adsorption was not very favorable to Cu (II), hence not all binding sites may be available to Cu(II). In addition to the correlation coefficient (r^2) and Standard Deviation (S.D.) for assessing the accuracy of estimation, the model can be displayed in terms of a dimensionless constant called separation factor R_L (also called equilibrium parameter) which is presented by this equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

Where K_L is the Langmuir constant which represents adsorption intensity (L/mg). In the range of initial concentrations of Cu (II) and Pb(II) from 100 to 1250 mg L⁻¹, the separation factor is from 0.13 to 0.65 and 0.0064 to 0.074, respectively. This data indicates that the copper and lead adsorption onto bentonite for various initial concentrations is favorable and reversible because

$0 < R_L < 1$ [10]. The high value of K_L in Pb(II) adsorption was a reason for the decrease of the separation factor and with an increase in the Pb(II) initial concentration, the separation factor approached to zero.

• *Freundlich isotherm model*

The Freundlich isotherm model describes the processes of non-ideal, multilayer adsorption on heterogeneous surfaces and assumes that the adsorption process is reversible. According to the presented linear form of equation in Table.1, the Freundlich isotherm has two

constants, K_F and $1/n$, which express the relative adsorption capacity and adsorption intensity (or surface heterogeneity), respectively. This parameter determined from an intercept and slope of a plot of $\ln q_e$ against $\ln C_e$. The value of these parameters (Table. 2) shows that $1/n$ is 0.35 and 0.14 for copper and lead adsorption onto bentonite, respectively. A $1/n$ between 0 and 1 indicate a favorable process and $1/n$ below unity implies a chemisorptions process. Accordingly, the Cu(II) and Pb(II) adsorption onto bentonite is favorable and chemisorption [19].

Table 1. Equations of different isotherm models.

models	Equation	Descriptions	ref
Two parameters:			
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m \cdot K_L} + \frac{C_e}{q_m}$	q_m maximum adsorption capacity (mg/g), K_L Adsorption intensity or Langmuir (L/mg).	[19]
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	K_F relative adsorption capacity ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$), n adsorption intensity	[19]
Temkin	$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$	A_T and b_T temkin constant that b_T is related to the heat of adsorption (J mol^{-1}), R gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), T absolute temperature (K)	[19]
Dubinin-Radushkevich	$\begin{aligned} \ln q_e &= \ln q_{\max} - \beta \varepsilon^2 \\ \varepsilon &= RT \ln(1 + 1/C_e) \\ E &= \frac{1}{\sqrt{2\beta}} \end{aligned}$	β activity coefficient related to sorption energy (mol^2/KJ^2), E free energy per molecule of adsorbate (KJ) which represent: — physical adsorption if $E < 8 \text{ kJ mol}^{-1}$ — chemical absorption or ion exchange if $8 < E < 16 \text{ kJ mol}^{-1}$ — particle diffusion if $E > 16 \text{ kJ mol}^{-1}$	[19]
Three parameter:			
Khan	$q_e = \frac{q_m b_K C_e}{(1 + b_K C_e)^{a_K}}$	b_K Khan constant, a_K Khan exponent	[21,22]

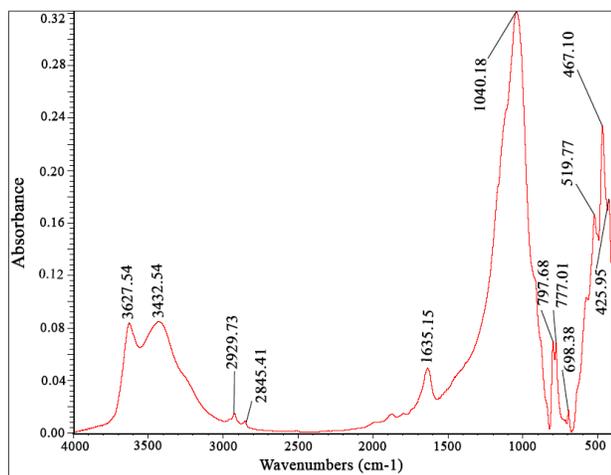


Fig. 2. FTIR spectrum of bentonite.

- *Temkin isotherm model*

The linear equation of the Temkin isotherm model is shown in Table 1. The binding energies of adsorbent-adsorbate interactions are assumed to be uniformly distributed, which causes a linear decrease in the heat of adsorption. On the other hand, the Temkin model has modified the Langmuir model by considering the effect of temperature in the adsorption processes. This isotherm equation has an A_T and a b_T constant which are determined from the intercept and slope of the linear plots of q_e versus $\ln C_e$ and are given in Table 2. The b_T constant is related to the heat of adsorption (J/mol) and A_T indicates the potential of adsorption. The amount of A_T , which are 0.1223 and 45.4028 for Cu(II) and Pb(II) respectively, confirms that the potential of Pb(II) adsorption is greater than the Cu(II) adsorption. However, the value of b_T represented that the heat of the Cu(II) adsorption was more than the Pb(II) adsorption onto bentonite.

Table 2. The isotherm model constants for Pb and Cu individual adsorption onto bentonite.

	model	parameter	Amount for Cu adsorption	Amount for Pb adsorption
Two parameter models	Langmuir	$q_m(\text{mg g}^{-1})$	21.097	57.803
		R^2	0.947	0.994
		R_L	0.13-0.65	0.006-0.074
		$K_L(\text{L mg}^{-1})$	0.005	0.125
	Freundlich	$S.D$	0.470	0.220
		$K_F(\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1})$	1.678	23.850
		$1/n$	0.346	0.142
		R^2	0.982	0.935
	Temkin	$S.D$	0.022	0.020
		$b_T(\text{J/mol})$	694.312	441.504
		$A_T(\text{L/mg})$	0.122	45.403
		R^2	0.902	0.897
Dubinin-Radushkevich	$S.D$	0.140	0.130	
	$q_m(\text{mg g}^{-1})$	27.990	72.167	
	$\beta(\text{mol}^2 \text{KJ}^{-1})$	5.00E-09	1.00E-09	
	$E(\text{KJ mol}^{-1})$	10	22.361	
	R^2	0.960	0.890	
Three parameter model	Khan	$S.D$	0.014	0.020
		q_m	0.609	9.856
		a_K	0.628	0.841
		b_K	10.117	163.040
		R^2	0.970	0.835

- *Dubinin-Radushkevich isotherm model*

The empirical Dubinin-Radushkevich model isotherm assumes homogenous surface adsorption [20] and its linear equation is given in Table.1. The q_{\max} and β are calculated from the intercepts and slopes of the linear plots of $\ln q_e$ versus ϵ^2 , respectively, and are given in Table 2. The calculated maximum adsorption capacity (q_{\max}) is 27.99 and 72.17 mg/g for Cu (II) and Pb(II) adsorption onto

bentonite, respectively, that is confirmed this parameter in the Langmuir isotherm. This model is usually applied to distinguish between physical and chemical adsorption of metal ions with the calculation of adsorption free energy. The adsorption free energy (E) is 10 and 22.36 kJ, respectively (Table 2), which means that the adsorption of Cu(II) onto bentonite is a chemical absorption or ion exchange process while the adsorption of Pb(II) onto bentonite is a particle diffusion process.

- *Khan isotherm model*

The Khan isotherm model is a three-parameter isotherm that was offered in 1997 for aromatic adsorption by activated carbon [21]. The equation of this model is presented in Table 1 which a_K and b_K are two constants and are provided in Table 2. The Khan isotherm equation also reflects the combined features of the Langmuir and Freundlich isotherm equations. When a_K verges to unity, it converges to the Langmuir isotherm. The equation can be converted to a Freundlich-type isotherm when the value of the term b_K becomes much greater than unity [22]. As shown in Table 2, a_K is 0.63 and 0.84 for Cu(II) and Pb(II) adsorption onto bentonite, respectively. It was seen that the Pb(II) adsorption verged to unity and the Khan isotherm model was approached to Langmuir for its adsorption onto bentonite. Thus, the parameters of these two models can be adapted to each other. The b_K parameter is related to binding energy, similar to K_L of Langmuir, so that the value of b_K confirmed that the Pb(II) adsorption performed better than Cu(II) onto the bentonite. Furthermore, the maximum adsorption capacity of the Khan isotherm is lower than the Langmuir model. According to these two models shown in Table 2, the Langmuir model with a higher correlation coefficient is better fitted to the experimental data than the Khan model and it is more acceptable.

Table 3. The isotherm model constants for Pb and Cu simultaneous adsorption onto bentonite.

model	parameter	Cu in presence of Pb	Pb in presence of Cu
Langmuir	$q_m(\text{mg/g})$	22.173	40.486
	R^2	0.968	0.995
	R_L	0.270-0.830	0.040-0.360
	$K_L(\text{L mg}^{-1})$	0.002	0.0175
Freundlich	S.D	0.330	0.164
	$K_F(\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1})$	0.472	6.089
	$1/n$	0.505	0.255
	R^2	0.983	0.966
Temkin	S.D	0.030	0.400
	$b_T(\text{J mol}^{-1})$	482.253	382.913
	$A_T(\text{L mg}^{-1})$	0.0183	0.531
	R^2	0.967	0.980
Dubinin-Radushkevich	S.D	0.130	0.037
	$q_m(\text{mg g}^{-1})$	31.649	59.531
	$\beta(\text{mol}^2/\text{KJ}^2)$	7.00E-09	3.00E-09
	$E(\text{KJ mol}^{-1})$	8.451	12.909
h	R^2	0.977	0.976
	S.D	0.010	0.012

3.5. Evaluation of individual Adsorption Isotherm Models of Cu and Pb onto bentonite

According to the results that are summarized in Table 2, it was found that the affinity for Pb(II) to interact with clay is greater than Cu(II). The regression coefficients r^2 values represent that the five isotherm models provide a good correlation for the sorption of the two metal ions. The good correlation coefficient confirms the monolayer adsorption of Pb(II) and multilayer adsorption of Cu(II) onto the surface of bentonite.

3.6. Equilibrium studies of Cu and Pb simultaneous adsorption onto bentonite

As mentioned in the experimental method section, Cu(II) and Pb(II) were mixed and the equilibrium adsorption was investigated similar to the individual adsorption. The results of these analysis were represented in Table 3. It demonstrated that the amount of Pb(II) adsorption in the presence of Cu(II) in comparison to its individual adsorption, decreased from 57.803 to 40.486. This indicates that in a mixture of these two ions, Cu(II) could inhibit the Pb(II) adsorption. However, the Cu(II) adsorption in the presence of the Pb(II) ion is a little more than the individual adsorption of Cu(II) onto bentonite. Generally, competition between Cu(II) and Pb(II) for adsorption onto Iranian bentonite has showed the following affinity order : Pb(II) > Cu(II), which has the same affinity as their adsorption onto Chinese natural bentonite [12]. When comparing the performance of Iranian bentonite with Turkish bentonite, the Iranian bentonite efficiency in Cu(II) and Pb(II) adsorption was much better than the Turkish bentonite [4]. Furthermore, according to the correlation coefficients which are presented in Table 3, similar to individual adsorption, Pb(II) adsorption in the presence of Cu(II) was fitted to the Langmuir model better than the Freundlich model. So, in the presence of Cu(II), only a monolayer of Pb(II) was adsorbed onto the bentonite. By the way, the adsorption of Cu(II) onto the bentonite in the presence of Pb(II) was a multilayer process. According to the adsorption free energy (E) of the Dubinin-Radushkevich model, the adsorption of Cu(II) in the presence of Pb(II) and also Pb(II) in the presence of Cu(II) onto the bentonite are a chemical adsorption or ion exchange process.

4. Conclusion

The removal of Cu(II) and Pb(II) by Iranian bentonite was investigated in an individual and simultaneous system by the batch adsorption technique. In comparing the individual adsorption of Cu(II) and Pb(II) onto bentonite, it was found that the affinity for Pb(II) to interact with bentonite was higher than Cu(II). The Pb(II) ion was adsorbed homogeneously in the monolayer process onto

the bentonite and the Cu(II) had multilayer adsorption on the heterogeneous surfaces of bentonite. The simultaneous system competition between Cu(II) and Pb(II) in adsorption onto the bentonite caused the adsorption capacity of Pb(II) to decrease from 57.803 mg/g to 40.49 mg/g; however, the adsorption of Cu(II) increased from 21.10 to 22.17 mg/g which showed that in the simultaneous system, Cu(II) can prevail over Pb(II) in adsorption onto the bentonite. In the simultaneous system, like the individual ones, the adsorption of Pb(II) was done homogeneously onto the bentonite in a monolayer process and Cu(II) had multilayer adsorption on the heterogeneous surfaces of the bentonite. Also, both of the adsorptions were done on a chemical absorption or an ion exchange process.

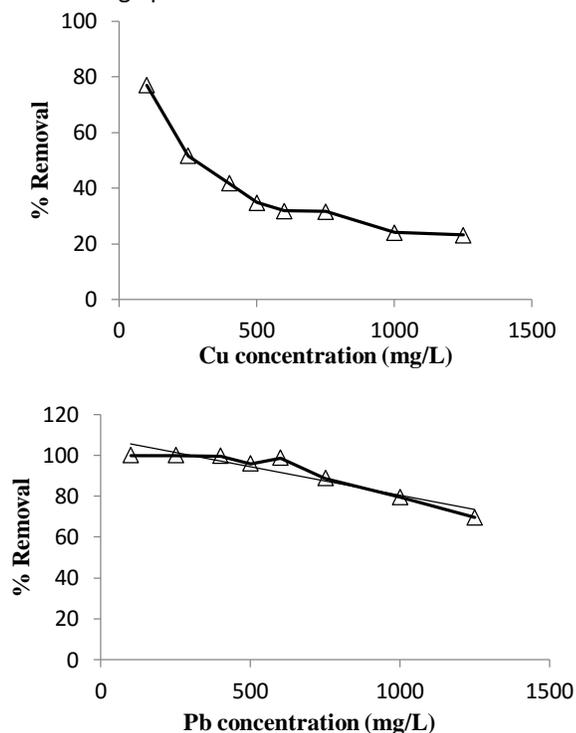


Fig. 3. Effect of Pb(II) and Cu(II) ion concentration on their adsorption onto bentonite, m/V: 15 g/L, T: 298 K, particle size: 150 μm , stirring speed: 600 rpm, contact time: 30 min.

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