

Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand

II. Equilibrium study and competitive adsorption

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Abstract

The adsorption equilibrium of MOCS and the Cu(II) and Pb(II) ions removal capacity by MOCS in single-(non-competitive) and binary-(competitive) component sorption systems from aqueous solutions were investigated. The equilibrium data were analyzed using the Langmuir, Freundlich, Temkin and Redlich–Peterson isotherms. The characteristic parameters for each isotherm were determined. The Langmuir and Redlich–Peterson isotherms provided the best correlation for both Cu(II) and Pb(II) onto MOCS. From the Langmuir isotherms, maximum adsorption capacities of MOCS towards Cu(II) and Pb(II) are determined at different temperature. The maximum adsorption capacity of Cu(II) and Pb(II) per gram MOCS in single component sorption systems were from 5.91 and 7.71 μmol to 7.56 and 9.22 μmol for the temperature range of 288–318 K, respectively. The order of affinity based on a weight uptake by MOCS was as follows: Pb(II) > Cu(II). The same behavior was observed during competitive adsorption that is in the case of adsorption from their binary solution. The thermodynamic parameters (ΔG° , ΔH° , and ΔS°) for Cu(II) and Pb(II) sorption on MOCS were also determined from the temperature dependence. This competitive adsorption showed that the uptake of each metal was considerably reduced with an increasing concentration of the other, the adsorption of Cu(II) being more strongly influenced by Pb(II) than vice versa due to the higher affinity of MOCS for the latter.

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1. Introduction

Manganese oxides are poorly crystalline oxides that are commonly found in manganese rich coatings. In the natural environment, trace metals, such as Ni, Mo, Cu, Zn, Pb, Cr and UO_2^{2+} [1–4], can be strongly associated with manganese oxides. Even in the presence of a large excess of indifferent electrolytes, anions of weak acids and weakly hydrolyzed cations are strongly adsorbed on manganese oxides surface. Because of the large surface area, and high affinity for metal ions, manganese oxides provided an efficient scavenging pathway for heavy metals in toxic systems. Manganese oxides is one kind of surface acidic oxides, whose pH_{pzc} (point of zero charge) value is about 1.5–4.5 [5] and the charge of the hydrous oxide depends on the pH of

the medium. Commonly, manganese oxide's surface charge is negative, and it can be used as an adsorbent to remove heavy metals from wastewater. However, pure manganese oxide as a filter media is not favorable for both economic reasons and unfavorable physical and chemical characteristics. Furthermore, the fine particle size of the metal oxides makes it very difficult to separate from the water phase or to infiltrate through. But coating manganese oxide to a media surface may provide an effective surface and may be a promising media for heavy metal removal from wastewater. Silica sand is a common conventional filter media because of its economy, inertness, and availability. Because of poor performance of plain silica sand for heavy metal adsorption and filtration, modifications are needed for wastewater treatment. The result of coating sand with a thin layer of manganese oxide can enhance sorption capacity for metal elements, as compared to plain filter sand. This enhanced capacity is a result of increased surface area and amphoteric surface charge the coating provides [6].

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The research described here was designed to test the properties of MOCS as an adsorbent for removing copper(II) and lead(II) from synthetic solutions in batch system. The adsorption capacities of MOCS for Cu(II) and Pb(II) was shown as a function of temperature and initial concentration. The paper also investigated the competitive effects between copper and lead ions on the sorption capability of MOCS in binary component systems and the obtained results were compared with the non-competitive data. The sorption phenomena in single component systems were expressed by the Langmuir, Freundlich, Temkin and Redlich–Peterson adsorption models and the effect of temperature on the model constants was investigated. The thermodynamics, such as ΔG° , ΔH° , and ΔS° have been calculated to determine adsorption mechanism.

1.1. Equilibrium parameters of adsorption

Equilibrium data, commonly known as adsorption isotherm, is important to develop an equation that accurately represents the results and can be used in design of sorption systems. Four adsorption models, such as Langmuir, Freundlich, Temkin and Redlich–Peterson, were used to describe the equilibrium between adsorbed metal ions on MOCS and metal ions in solution at a constant temperature. The Langmuir model [7], which is valid for monolayer adsorption onto a surface containing a finite number of identical sites, is probably the most popular isotherm model due to its simplicity and its good agreement with experimental data. It could be described by the linearized form:

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

where q_{\max} (mmol g⁻¹) is the maximum amount of metal ion per unit weight of MOCS and K_a is the equilibrium adsorption constant. C_e is the equilibrium metal ion concentration in mmol l⁻¹ and q_e is the adsorption equilibrium metal ion uptake capacity in mmol g⁻¹. By plotting C_e/q_e versus C_e , q_{\max} and K_a can be determined.

According to the Freundlich equation [8], the amount of substance adsorbed per gram of adsorbent (q_e) is related to the equilibrium concentration (C_e) by the equation as follows:

$$q_e = K_F C_e^{1/n} \quad (2)$$

and the equation may be linearized by taking logarithms:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mmol g⁻¹), C_e is the equilibrium concentration of solute in the bulk solution (mmol l⁻¹), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mmol g⁻¹) and $1/n$ is the constant indicative of the intensity of the adsorption.

The Temkin isotherm equation [9] describes the behavior of many adsorption systems on heterogeneous surface and it

is based on the following equation:

$$q_e = \frac{RT \ln(a_t C_e)}{b_t} \quad (4)$$

The linear form of Temkin isotherm can be expressed by Eq. (4):

$$q_e = A + B \ln C_e \quad (5)$$

where R is the general gas constant, T absolute temperature (K), A ($= \frac{RT}{b_t} \ln a_t$) and B ($= \frac{RT}{b_t}$) represents isotherm constants, respectively.

The Redlich–Peterson isotherm [10] contains three parameters and the form of equation includes features of the Langmuir and the Freundlich isotherms. Its non-linear equation is expressed as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (6)$$

This equation reduces to a linear isotherm at low surface coverage, to the Freundlich isotherm at high adsorbate concentration, and to the Langmuir isotherm when $g = 1$ [11]. However, the equation cannot be linearized for easy estimation of isotherm parameters. The linearization of the expression gives

$$\ln \left(\frac{AC_e}{q_e} - 1 \right) = g \ln C_e + \ln B \quad (7)$$

where A , B , and g are the Redlich–Peterson parameters. g lies between 0 and 1.

The two-parameter models, namely Langmuir, Freundlich and Temkin can be readily linearized and hence the parameter values can be easily obtained using the linear least square technique. However, for three-parameter model, such as Redlich–Peterson model, the parameter values can be evaluated from the linear plot using a trial and error optimization method according to Eq. (7). All the data points for Cu(II) and Pb(II) were used in estimating the parameter values. Subsequently, with these values the percentage deviation based on the predicted value in Cu(II) and Pb(II) for each isotherm model were calculated. The percent deviation was calculated as

$$\% \text{ deviation} = \left[\frac{q_{\text{exp}} - q_{\text{theo}}}{q_{\text{theo}}} \right] \times 100 \quad (8)$$

1.2. Thermodynamic parameters of adsorption

In order to explain the effect of temperature on the adsorption thermodynamic parameters, standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) were determined.

The adsorption process of metal ions can be summarized by the following reversible process which represents a heterogeneous equilibrium. The apparent equilibrium constant (K'_c) of the adsorption is defined as [12,13]:

$$K'_c = \frac{C_{\text{ad,e}}}{C_e} \quad (9)$$

where $C_{ad,e}$ is the concentration of metal ion on the adsorbent at equilibrium. In this case the activity should be used instead of concentration in order to obtain the standard thermodynamic equilibrium constant (K_c^0) of the adsorption system. If infinite dilution value of K_c' can be found by calculating the apparent equilibrium constant (K_c') at different initial concentrations of metal ion and extrapolating to zero, this value will give K_c^0 . The K_c^0 value is used in the following equation to determine the Gibbs free energy of adsorption (ΔG°) [12,13]:

$$\Delta G^\circ = -RT \ln K_c^0 \quad (10)$$

The enthalpy (ΔH°) and entropy (ΔS°) can be obtained from the slope and intercept of a van't Hoff equation of ΔG° versus T :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

where R is the gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is absolute temperature, K , and K_c' is equilibrium constant at the temperature T , respectively. The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption.

2. Materials and methods

2.1. Adsorbent

The quartz sand was provided from Zhengzhou's Company of tap water in China. The diameter of the sand was ranged in size from 0.99 to 0.67 mm. The sand was soaked in 0.1 mol l^{-1} hydrochloric acid solution for 24 h, rinsed with distilled water and dried at 373 K in the oven in preparation for surface coating. Manganese oxide coated sand was accomplished by utilizing a reductive procedure modified to precipitate colloids of manganese oxide on the media surface. A boiling solution containing potassium permanganate was poured over dried sand placed in a beaker, and hydrochloric acid (37.5%, $W_{\text{HCl}}/W_{\text{H}_2\text{O}}$) solution was added drop-wise into the solution. After stirring for 1 h, the media was filtered, washed to pH 7.0 using distilled water, dried at room temperature, and stored in polypropylene bottle for future use.

2.2. Metal solutions

All chemicals and reagents used for experiments and analyses were of analytical grades. Stock solutions of 2000 mg l^{-1} Cu(II) and Pb(II) were prepared from $\text{Cu}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ in distilled, deionized water containing a few drops of concentrated HNO_3 to prevent the precipitation of Cu(II) and Pb(II) by hydrolysis. The solutions were diluted as required to obtain working solutions in the range of 0.077 – 1.27 mmol l^{-1} of Cu(II) and 0.097 – 1.54 mmol l^{-1} of Pb(II), respectively. The initial pH of the working solution was adjusted by addition of HNO_3 or NaOH solution.

2.3. Methods of adsorption studies

Batch adsorption studies were conducted by shaking the flasks at 120 rpm for a period of time using a water bath cum mechanical shaker. Following a systematic work on the sorption uptake capacity of Cu(II) and Pb(II) in batch system and the ionic competition effect on sorption were studied in the present work.

For the equilibrium study, a known mass of MOCS added to a fixed volume of sample solution containing varying concentrations and the temperature was controlled with a water bath at the temperature ranged from 288 to 318 K for the studies. When reached the sorption equilibrium (180 min), filtrated to separate MOCS and the solution. The concentration of the free metal ions in the filtrate was analyzed using flame atomic absorption spectrometer (AAS) (AAAnalyst 300, Perkin-Elmer). Competitive adsorption of Cu(II) and Pb(II) ions from their binary solutions was investigated by following a similar procedure as described above. The uptake of the metal ions in single and binary systems was calculated by the difference in their initial and final concentrations. Each experiment was repeated three times and the results given were the average values.

The data obtained in batch model studies was used to calculate the equilibrium metal uptake capacity. It was calculated for each sample of copper and lead ions by using the following expression:

$$q_e = \frac{v(C_0 - C_e)}{m} \quad (12)$$

where q_e is MOCS adsorption equilibrium metal ion uptake capacity in mmol g^{-1} , v the sample volume in l, C_0 is the initial metal ion concentration in mmol l^{-1} , C_e is the equilibrium metal ion concentration in mmol l^{-1} , and m is the weight of MOCS in g.

3. Result and discussion

3.1. Effect of initial concentration of Cu(II) and Pb(II) sorption on temperature-dependent adsorption

A volume of 20 ml of Cu(II) and Pb(II) solution with initial concentrations ranged from 0.077 to 1.27 mmol l^{-1} and 0.097 to 1.54 mmol l^{-1} were placed in 125 ml conical flasks, respectively. The initial pH was 4.0. An accurately weighed MOCS sample (20 g l^{-1}) with particle size range from 0.99 to 0.67 mm was then added to the solution. In order to prevent solution evaporation, each conical flask using in the experiments was sealed. After shaking the flasks for 180 min at the temperature range from 288 to 318 K, the filtrates were analyzed for the remaining copper and lead ion concentrations, respectively. The capacities of adsorption of Cu(II) and Pb(II) on MOCS are shown in Fig. 1.

The adsorption capacities of the MOCS increased rapidly first with the increasing of the initial concentration of Cu(II) and Pb(II) and reached a saturation values of around 0.40 and 0.45 mmol l^{-1} of Cu(II) and Pb(II), respectively. And higher removals for Cu(II) and Pb(II) were observed in the higher temperature range. This was due to the increasing tendency of

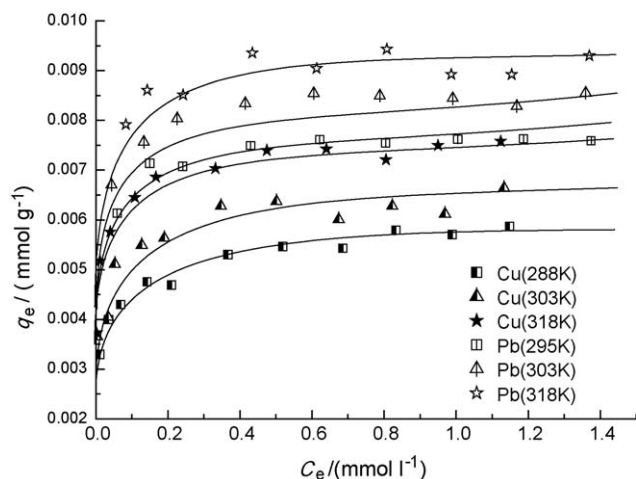


Fig. 1. Effect of Cu(II) and Pb(II) concentrations on the adsorption of Cu(II) and Pb(II) on MOCS from aqueous solutions at initial pH 4.0 at different temperatures.

adsorbate ions to adsorb from the solution to the interface with increasing temperature. The increase of the equilibrium uptake at increased temperature indicated that the adsorption of Cu(II) and Pb(II) ions to MOCS is endothermic in nature.

3.2. Determination of equilibrium model constants

In order to optimize the design of an adsorption system to remove Cu(II) and Pb(II) from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curves. The Langmuir, Freundlich, Temkin and Redlich–Peterson models are often used to describe equilibrium sorption isotherm. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanisms and the surface properties and affinities of the adsorbent.

The linearized form of Langmuir, Freundlich, Temkin and Redlich–Peterson adsorption isotherms obtained at the temperatures of 288, 295, 303 and 318 K are given in Figs. 2–5,

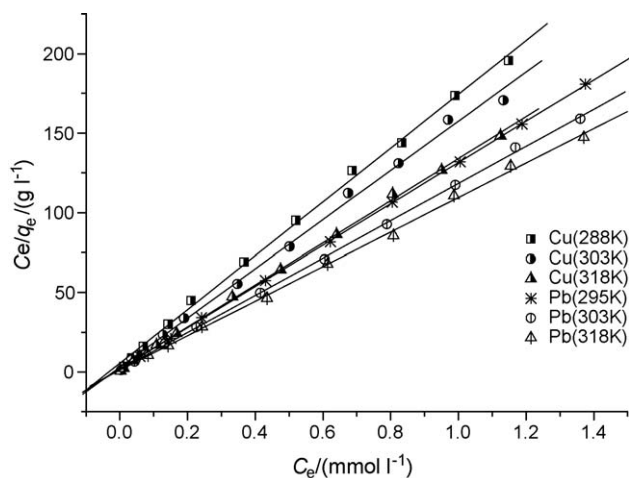


Fig. 2. Langmuir adsorption isotherms of Cu(II) and Pb(II) by MOCS at different temperatures.

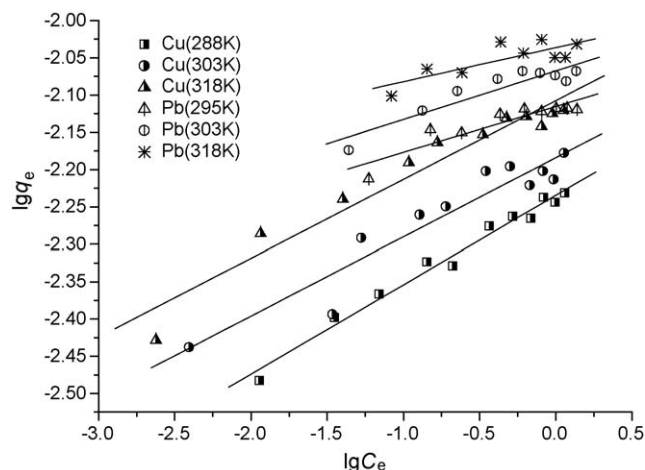


Fig. 3. Freundlich adsorption isotherms of Cu(II) and Pb(II) by MOCS at different temperatures.

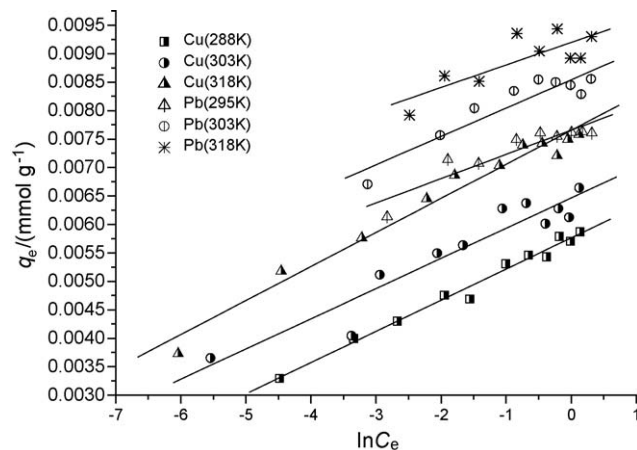


Fig. 4. Temkin adsorption isotherms of Cu(II) and Pb(II) by MOCS at different temperatures.

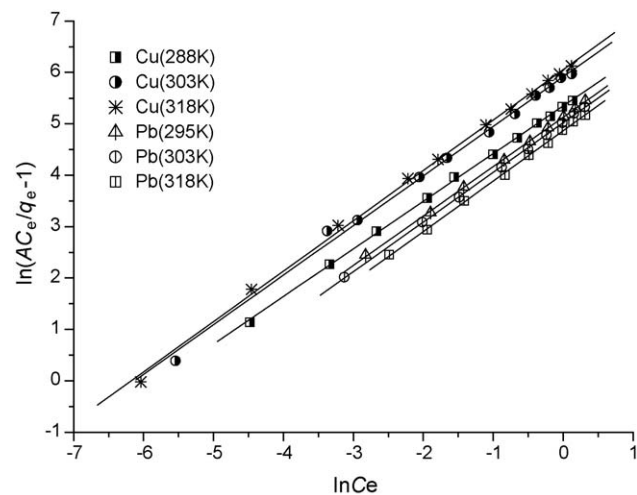


Fig. 5. Redlich–Peterson adsorption isotherms of Cu(II) and Pb(II) by MOCS at different temperatures.

Table 1
Langmuir, Freundlich, Redlich–Peterson and Temkin parameters for adsorption of Cu(II) and Pb(II) onto MOCS

Isothermal model parameters	Cu(II)			Pb(II)		
	288 K	303 K	318 K	295 K	303 K	318 K
Langmuir						
K_a (l mmol^{-1})	31.2	53.1	74.3	69.76	84.17	95.94
q_m (mmol g^{-1}) $\times 10^{-3}$	5.91	6.47	7.56	7.71	8.55	9.22
R	0.999	0.998	1.00	1.00	1.00	0.999
R_L	0.0248	0.0147	0.0106	0.00930	0.00772	0.00678
Freundlich						
K_F (mmol g^{-1}) $\times 10^{-3}$	5.83	6.55	7.81	7.66	8.55	9.20
$1/n$	0.120	0.106	0.106	0.061	0.065	0.046
R	0.991	0.952	0.970	0.909	0.926	0.807
Temkin						
$A \times 10^{-3}$	5.76	6.46	7.65	7.65	8.54	9.19
$B \times 10^{-4}$	5.48	5.31	5.98	4.25	4.98	3.95
R	0.993	0.953	0.986	0.918	0.931	0.820
Redlich–Peterson						
A	1.2	2.3	3.1	1.3	1.3	1.2
B	210	370	426	169	152	130
g	0.927	0.965	0.980	0.961	0.966	0.980
R	1.00	0.998	0.999	1.00	1.00	1.00

respectively, whereas Table 1 presents the correspondent constants along with the coefficients of correlation (R) and percent deviation associated at each linearized model according to Eqs. (1), (3), (5) and (7).

The experimental equilibrium data of Cu(II) and Pb(II) were also compared with the theoretical equilibrium data obtained from these adsorption models. The values of percent deviation (Figs. 6 and 7) also confirmed that the adsorption equilibrium data fitted well to the Langmuir and Redlich–Peterson models in this studied conditions.

The values of q_{\max} and K_a for different temperatures were calculated from the Langmuir plots and the results are tabulated in Table 1. These isotherms were found to be linear over the entire concentration range studied with extremely high R values for Cu(II) and Pb(II), respectively. The R values suggest

that the Langmuir isotherm provides a good model of the sorption system. Langmuir constant, q_{\max} , represents the monolayer saturation at equilibrium. The maximum capacity q_{\max} determined from the Langmuir isotherm defines the total capacity of MOCS for Cu(II) and Pb(II). The maximum capacity of MOCS in this studies for Cu(II) and Pb(II) were obtained at 318 K, a slight increase being observed with the increase in sorption temperature. The other mono-component Langmuir constant K_a , corresponds to the concentration at which a Cu(II) or Pb(II) ion amount of $q_{\max}/2$ is bound and indicates the affinity for the binding of Cu(II) and Pb(II) ions. A high K_a value indicates a high affinity. The values of K_a , increased with increasing of temperature, indicating that the affinity of MOCS for Cu(II) and Pb(II) increase as the temperature of sorption increase, which may be

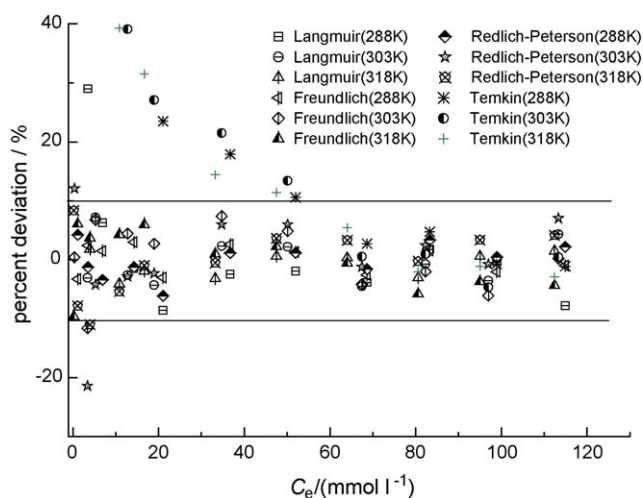


Fig. 6. Comparison of experimental and predicted amount of Cu(II) adsorbed on MOCS at different temperatures.

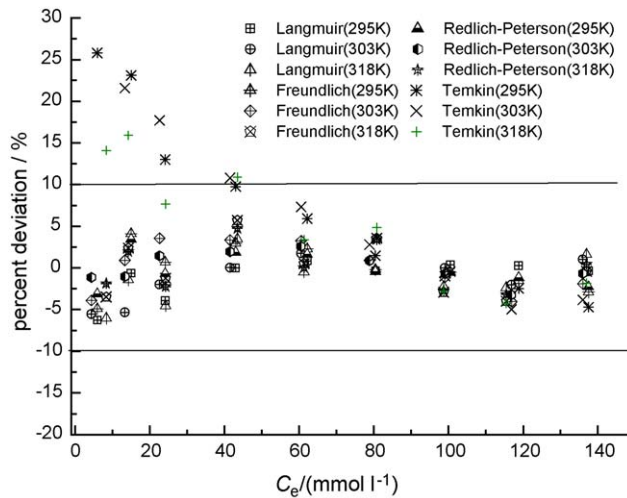


Fig. 7. Comparison of experimental and predicted amount of Pb(II) adsorbed on MOCS at different temperatures.

mainly due to the increase in number of active sites caused by the breaking of some bonds.

The Freundlich model does not describe the saturation behavior of adsorbent. The constant K_F indicates the sorption capacity of the sorbent. The values of K_F and n determined from the Freundlich plots changed slightly with the rise in temperature. As the constant n at equilibrium were bigger than 1, indicating that metal ions were favorably adsorbed by MOCS at all the temperatures studied [12]. These results indicated that MOCS had a very strong adsorption capacity for Cu(II) and Pb(II) in the solution.

The corresponding Temkin parameters of A and B at different temperatures are also given in Table 1 for Cu(II) and Pb(II) system. The constant A also increased with temperature increasing.

The Redlich–Peterson isotherm plots (Fig. 5) for sorption of the Cu(II) and Pb(II) on MOCS showed that the Redlich–Peterson isotherm accurately described the sorption behaviors of metal ions on MOCS over the concentration ranges studied. The parameters of the equation did not exhibit any tendencies of the changes with the experimental factors. However, the exponent, g , for all samples was close to 1, showing the closeness of the model to the Langmuir isotherm.

As shown in Table 1, it can be concluded that equilibrium data fitted very well to all the equilibrium models in the studied concentration range of Cu(II) and Pb(II) at all the temperatures studied according to the values of correlation coefficients (R) except Freundlich and Temkin model for Pb(II). The comparison of the values of R indicates that Langmuir and Redlich–Peterson isotherms best fits the experimental range studied, since it presents the greater coefficients of correlation at all temperatures. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on MOCS surface, since the Langmuir equation assumes that the surface is homogenous [14]. The values of q_{\max} obtained from the Langmuir isotherm equation for Pb(II) adsorption on MOCS was greater than that of Cu(II) at all the temperature, which is indicated that the functional groups on the surface of MOCS had a relatively stronger affinity for Pb(II) than Cu(II) and potential of the adsorption for Cu(II) and Pb(II) on MOCS was in the following order: Pb(II) > Cu(II).

For adsorption of Cu(II) and Pb(II) to MOCS, the experimental and predicted q_e values with deviation percents are presented in Figs. 6 and 7. The percent magnitude of absolute deviation was changed from 0% to 12% and 0% to 10% for Cu(II) and Pb(II) in Langmuir, Freundlich and Redlich–Peterson models, respectively. The correlations between experimental and calculated results for each model were acceptable at moderate initial concentrations; however, a very low concentrations, the correlation deviation slightly. This could be explained by the experimental and measurement errors found at very low concentrations. Figs. 6 and 7 also showed that at higher concentrations, the absolute deviation percents found from the Langmuir, Freundlich and Redlich–Peterson model were higher than that of Temkin model. In view of the values of percentage deviation in Figs. 6 and 7, it appears that the Langmuir, Freundlich and Redlich–Peterson models provides the most satisfactory representation of the data in the studied concentration range at almost all temperatures.

The effect of isotherm shape can be used to predict whether a sorption system is ‘favorable’ or ‘unfavorable’. One of the essential characteristics of Langmuir equation could be expressed by dimensionless constant called equilibrium parameter, R_L [15]:

$$R_L = \frac{1}{1 + K_a C_0} \quad (13)$$

where C_0 is the highest initial solute concentration (mmol l^{-1}). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). It is shown that the sorption of Cu(II) and Pb(II) ions on MOCS is very favorable at all temperatures studied (Table 1). The R_L values also indicated that sorption is more favorable for higher temperature than for the lower ones. It is obvious that MOCS is a good sorbent for removing Cu(II) and Pb(II) ions from solution.

3.3. Thermodynamic parameters of adsorption

The K_c^0 value evaluated from the $C_{\text{ad,e}}/C_e$ versus C_e plot (data not shown) was used to find the ΔG° value. The standard Gibbs free energy (ΔG°) was obtained at different temperature according Eq. (10). The standard enthalpy (ΔH°) and entropy changes (ΔS°) of sorption determined from the ΔG° versus T plot according to Eq. (11). The thermodynamic parameters of ΔG° , ΔH° and ΔS° were shown in Table 2.

Positive values of ΔH° suggest the endothermic nature of the adsorption of Cu(II) and Pb(II) on MOCS. The negative values of ΔG° at various temperatures indicated the feasibility of the process and spontaneous nature of the adsorption. However, the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of Cu(II) and Pb(II) were inversely proportional to the temperature. Enhancement of adsorption capacity of adsorbent at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface. The positive values of ΔS° reflect the affinity of MOCS for Cu(II) and Pb(II) and show the increasing randomness at the solid/liquid interface during the sorption of metal ions on MOCS.

Table 2
Thermodynamic parameters for the adsorption of Cu(II) and Pb(II) at various temperatures by MOCS

Metal ion	T (K)			
	288	295	303	318
Cu(II)				
ΔG° (kJ mol ⁻¹)	-16.0		-17.7	-19.4
ΔH° (kJ mol ⁻¹)			17.1	
ΔS° (J mol ⁻¹ k ⁻¹)			115	
Pb(II)				
ΔG° (kJ mol ⁻¹)		-16.2	-17.1	-18.9
ΔH° (kJ mol ⁻¹)			18.2	
ΔS° (J mol ⁻¹ k ⁻¹)			117	

3.4. Competitive adsorption in binary metal system

In this group of experiments, competitive adsorption of Cu(II) and Pb(II) ions from their binary solutions was investigated by following a similar procedure as described above. These studies were performed at an initial pH of 4.0 at 293 K. The experiments of competitive adsorption of Cu(II) and Pb(II) included two parts: (i) the competitive adsorption of Cu(II) and Pb(II) in the total concentration was changeless; (ii) the effect on adsorption of Cu(II) with the presence of Pb(II) in the solution, and the effect on adsorption of Pb(II) with the presence of Cu(II) in the solution.

3.4.1. The competitive adsorption of Cu(II) and Pb(II) in the total concentration changeless

The objective of this part work was to study the effect of two metal ions coexistence on the total adsorptive capacity of MOCS. The experiment was carried out keeping the total concentration changeless (1.0 mmol l^{-1}) and changed each metal ions concentration. The result was shown in Fig. 8.

As shown in Fig. 8, values of the adsorption capacities q_e obtained from the experiment results for the binary-component system at described conditions were ranging from 0.162 to $2.94 \mu\text{mol g}^{-1}$ and 2.82 to $7.14 \mu\text{mol g}^{-1}$ for Cu(II) and Pb(II), respectively, which were less than those for the single-component solutions ($5.70 \mu\text{mol g}^{-1}$ for Cu(II) and $7.62 \mu\text{mol g}^{-1}$ for Pb(II)). However, the total adsorption capacity for these two metals in binary system exceeded the capacity than that of Cu(II) but less than that of Pb(II) in single-component systems. One type of the metal ion present interfered with the uptake of another one in the system, and the overall total metal uptake was slightly lower. It is indicated that the functional groups on the surface of MOCS had a relatively stronger affinity for Pb(II) than Cu(II) and potential of the adsorption for Cu(II) and Pb(II) on MOCS was in the following order: Pb(II) > Cu(II).

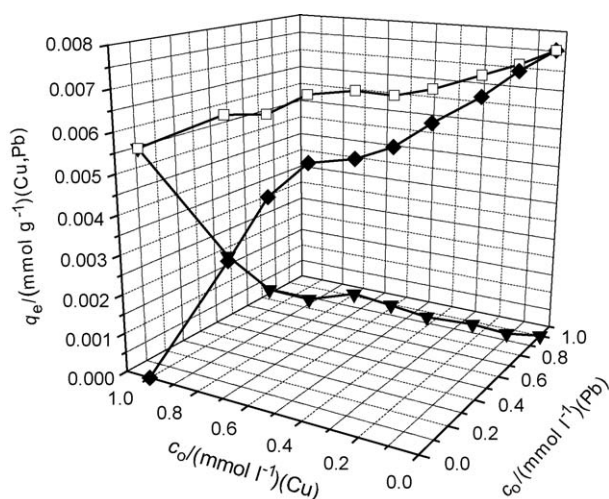


Fig. 8. Effect of the fixed total initial concentration of Cu(II) and Pb(II) on the adsorption capacity of each metal ions. (\square) q_e Pb(II); (\blacktriangledown) q_e Cu(II); (\blacksquare) q_e Cu(II) + Pb(II).

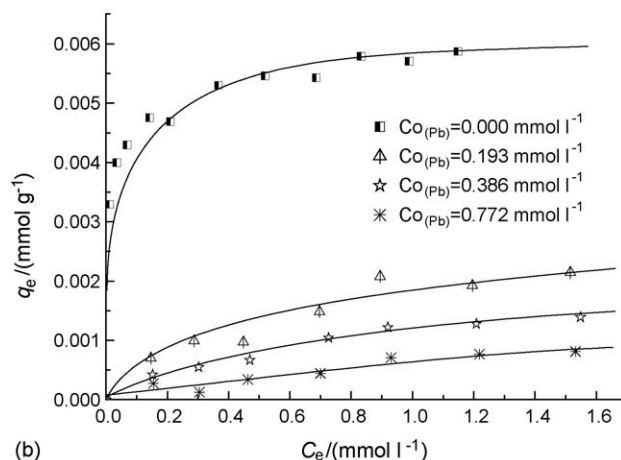
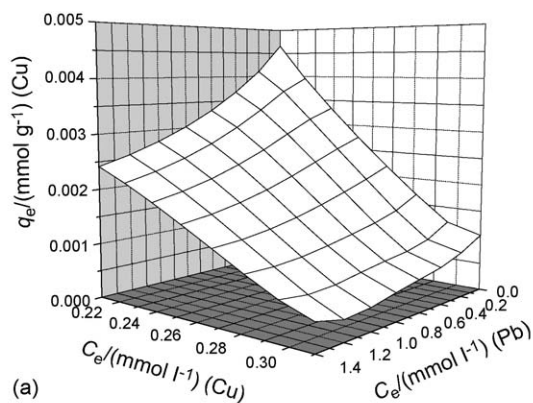


Fig. 9. (a) Two-metal sorption isotherm. The adsorption capacity of Cu(II) is plotted as a function of the equilibrium concentrations of Cu(II) and Pb(II). (b) Adsorption isotherms of Cu(II) in single- and binary-component sorption systems.

3.4.2. The effect on adsorption of Cu(II) or Pb(II) with the presence of Pb(II) or Cu(II) in the solution

In a series of two metal ions solution, the initial concentration of Cu(II) was fixed to $0.315 \text{ mmol l}^{-1}$, whereas, the concentration of Pb(II) were varied from 0 to 1.54 mmol l^{-1} . In another binary system, the initial concentration of Pb(II) was constant in $0.386 \text{ mmol l}^{-1}$, and the concentration of Cu(II) were varied from 0 to 1.57 mmol l^{-1} . In Figs. 9a and 10a, the two (equilibrium) metal concentrations were plotted against the Cu(II) or Pb(II) uptakes, respectively. As shown in Figs. 9a and 10a, when both Cu(II) and Pb(II) were present in the solution together, some reduction of the Cu(II) or Pb(II) uptake could be observed with increasing Pb(II) or Cu(II) concentration. The effect of Pb(II) on the adsorption uptake of Cu(II) was seen in Fig. 9a showing that the interference of Pb(II) with the Cu uptake was much more pronounced. The adsorption capacities $q_e(\text{Cu})$ decreased from 4.68 to $0.359 \mu\text{mol g}^{-1}$ and the maximum adsorption efficiency of Cu(II) was reduced 92.3% in the presence of Pb(II) (concentration ranging from 0 to 1.54 mmol l^{-1}). Conversely, as shown in Fig. 10a, whereas in the one-metal Pb system the Pb uptake was $7.57 \mu\text{mol g}^{-1}$ of MOCS at initial concentration $C_0[\text{Pb}] = 0.386 \text{ mmol l}^{-1}$, when 1.57 mmol l^{-1} (initial concentration) Cu(II) was present in the system, the Pb(II) uptake

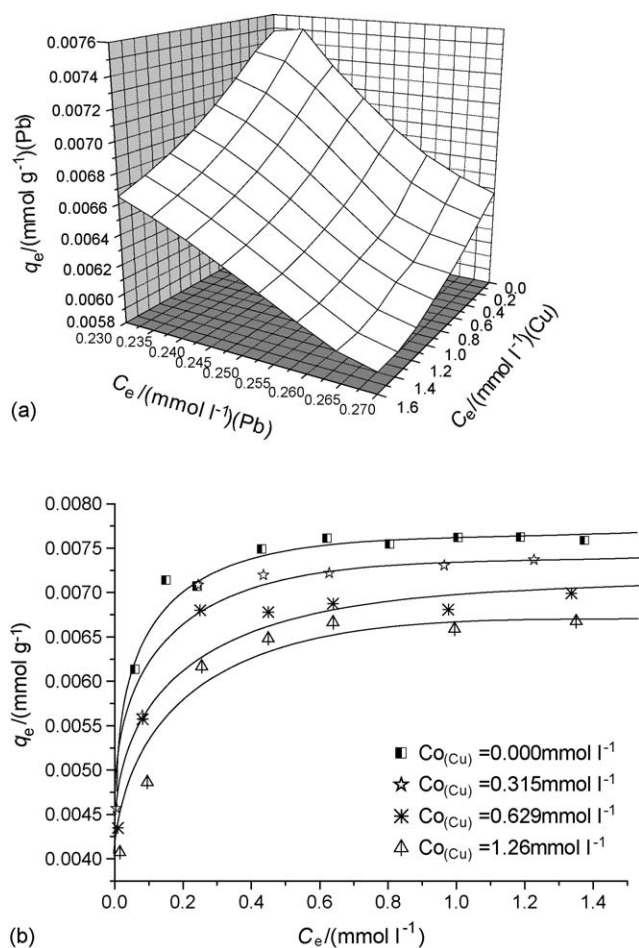


Fig. 10. (a) Two-metal sorption isotherm. The adsorption capacity of Pb(II) is plotted as a function of the equilibrium concentrations of Cu(II) and Pb(II). (b) Adsorption isotherms of Pb(II) in single- and binary-component sorption systems.

decreased to $5.92 \mu\text{mol g}^{-1}$ or 21.7% of the original value. A slightly reduction in the Pb uptake was observed even at relatively high Cu(II) concentrations. The result showed that Pb(II) had best affinity to MOCS than Cu(II). As MOCS was less favorable for Cu(II), Pb(II) added competed adsorption sites with Cu(II). As a result, addition of stronger binding metal ions, such as Pb(II), could weaken the chemical bonds between the functional group and weaker metal ions, such as Cu(II).

The effect of different levels of Pb(II) on the adsorption uptakes of Cu(II) was quantitatively much better demonstrated in Fig. 9b, which showed a comparison of the adsorbed quantity of Cu(II) per unit weight of MOCS at equilibrium between the solutions with Cu(II) ions present as the single metal and with the presence of increasing concentration of Pb(II) ions. Similarly and conversely, the effect of Cu(II) on the adsorption uptake of Pb(II) was seen in Fig. 10b. From Figs. 9b and 10b, a significant reduction in the Cu(II) uptake was observed even at relatively low Pb(II) concentration, however, slightly reduction in the Pb(II) uptake at relatively high Cu(II) concentration. Adsorption affinity of the tested metals is Pb(II) > Cu(II) which is the same affinity as indicated from the results under non-

Table 3

Some physical and chemical properties of the two ions

Properties	Cu(II)	Pb(II)
Ionic radius	0.72	1.20
Coordination number	2, 4	4, 6
Electron configuration	[Ar]3d ⁹	[Xe]4f ¹⁴ 5d ¹⁰ 6s ²
Electronegativity of the atom	1.90	2.33
Covalent index = $X_m^2(r + 0.85)$	5.67	11.1
Effective radius in solution	6.0	4.5

competitive conditions. This observation is in agreement with that reported by other studies [16].

The observed affinity in the sorption of Pb(II) and Cu(II) could be attributed to the difference in their class behavior on the basis of their covalent indices. Pb(II) is classified as a class b ion, while Cu(II) is classified as borderline ions. On the basis of this argument, it is possible to explain clearly the competition effects observed in the present study. Since Pb(II) belongs to a different class of ions (class b), other cations do not exert any effect on its sorption [17].

A covalent index for the class behavior of the metal ions. Covalent index is computed using the equation [18]:

$$\text{covalent index} = X_m^2(r + 0.85) \quad (14)$$

where X_m represents the electronegativity of the ion; r the ionic radius and 0.85 a constant assumed to reflect ionic radius of O and N donor atoms. In general, the greater the covalent index greater is the class b character and consequently its potential to form covalent bonds with adsorbent ligands.

As evident from Table 3, the covalent index of the two metals lie in the series Pb(II) > Cu(II). Consequently, affinity of the adsorbent also lies in the series Pb(II) > Cu(II). Similar covalent series for cation adsorption has been reported by Heidmann [19].

4. Conclusion

In this study, the adsorption potential of MOCS was investigated for the removal of Cu(II) and Pb(II) from single (non-competitive) and binary (competitive) aqueous systems. The adsorption isotherms of Cu(II) and Pb(II) onto MOCS were studied at different temperatures. The following results were obtained:

- The Langmuir, Freundlich, Temkin and Redlich–Peterson adsorption models were used for the mathematical description of the adsorption equilibrium of Cu(II) and Pb(II) onto MOCS. Results showed that the adsorption equilibrium data fitted very well to Langmuir and Redlich–Peterson isotherms in the studied concentrations range at all the temperatures studied.
- Cu(II) and Pb(II) adsorption capacity of MOCS increased with an increasing of temperature. The maximum adsorption capacities of Cu(II) and Pb(II) per gram MOCS were calculated as from 5.91 and 7.71 μmol to 7.56 and 9.22 μmol for the temperature range of 288–318 K, respectively.

- Thermodynamic constants were evaluated using equilibrium constants changing with temperature. The negative values of ΔG° indicated the spontaneity and the positive values of ΔH° and ΔS° showed the endothermic nature and irreversibility of Cu(II) and Pb(II) sorption, respectively.
- In binary system, the total adsorption capacity exceeded the capacity of Cu(II) but less than that of Pb(II) in single-component systems. Adsorption affinity of the tested metals is Pb(II) > Cu(II) which is the same affinity as indicated from the results under non-competitive conditions.

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References

- [1] H. Tamura, N. Katayama, R. Furrich, The Co^{2+} adsorption properties of Al_2O_3 , Fe_2O_3 , Fe_3O_4 , TiO_2 , and MnO_2 evaluated by modeling with the Frumkin isotherm, *J. Colloid Interf. Sci.* 195 (1997) 192–202.
- [2] G. Fu, H.E. Allen, C.E. Cowan, Adsorption of cadmium and copper by manganese oxide, *Soil Sci.* 152 (2) (1991) 72–81.
- [3] J.G. Catts, D. Langmuir, Adsorption of Cu, Pb, and Zn by $\delta\text{-MnO}_2$: applicability of the side binding-surface complexation model, *Appl. Geochem.* 1 (1986) 255–264.
- [4] A. Birsen, A.D. Timothy, Application of MnO_2 coated scintillating and extractive scintillating resins to screening for radioactivity in groundwater, *Nucl. Instrum. Meth. Phys. Res. A* 505 (2003) 458–461.
- [5] S.B. Kanungo, K.M. Paroda, Interfacial behavior of some synthetic MnO_2 samples during their adsorption of Cu^{2+} and Ba^{2+} from aqueous solution at 300 K, *J. Colloid Interf. Sci.* 98 (1984) 252–260.
- [6] J.J. Sansalone, Adsorptive – infiltration of metals in urban drainage – media characteristics, *Sci. Total Environ.* 235 (1999) 179–188.
- [7] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [8] H.M.F. Freundlich, Über die adsorption in lasungen, *Z. Phys. Chem.* 57 (1906) 385–470.
- [9] E. Guibal, I. Saucedo, J. Roussy, Uptake of uranyl ions by new sorbing polymers: discussion of adsorption isotherms and pH effect, *React. Polym.* 23 (1994) 147–156.
- [10] O. Redlich, D.L. Peterson, A useful adsorption isotherm, *J. Phys. Chem.* 63 (1959) 1024.
- [11] Y.S. Ho, J.F. Porter, G. McKay, *Water Air Soil Pollut.* 141 (2002) 1–33.
- [12] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of lead(II) ions onto *Chlorella vulgaris*, *Process Biochem.* 38 (2002) 89–99.
- [13] C. Namasivayam, K. Ranganathan, Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater, *Environ. Pollut.* 82 (1993) 255–261.
- [14] M. Özacar, Adsorption of phosphate from aqueous solution onto alunite, *Chemosphere* 51 (2003) 321–327.
- [15] C. Namasivayam, R.T. Yamuna, Adsorption of chromium(VI) by a low-cost adsorbent: biogas residual slurry, *Chemosphere* 30 (1995) 561–578.
- [16] R.M. McKenzie, The adsorption of lead and other heavy metals on oxides of manganese and iron, *Aust. J. Soil Res.* 18 (1980) 61–73.
- [17] M. Iqbal, R.J.I. Edyvean, Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of *Phanerochaete chrysosporium*, *Miner. Eng.* 17 (2004) 217–223.
- [18] E. Nieboer, W.A.E. McBryde, Free-energy relationships in coordination chemistry. III. A comprehensive index to complex stability, *Can. J. Chem.* 51 (1973) 2512–2524.
- [19] I. Heidmann, I. Christl, C. Leu, R. Kretzschmar, Competitive sorption of protons and metal cations onto kaolinite: experiments and modeling, *J. Colloid Interf. Sci.* 282 (2005) 270–282.