

Copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite

Runping Han^{a,*}, Weihua Zou^b, Hongkui Li^c, Yanhu Li^c, Jie Shi^a

^a Department of Chemistry, Zhengzhou University, No 75 of Daxue North Road, Zhengzhou 450052, PR China

^b College of Chemical Engineering, Zhengzhou University, No 97 of Wenhua Road, Zhengzhou 450002, PR China

^c School of Architectural Engineering of Henan Province, No 199 of Zhongyuan Middle Road, Zhengzhou 450007, PR China

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Abstract

The ability of manganese oxide coated zeolite (MOCZ) to adsorb copper and lead ions in single- (non-competitive) and binary- (competitive) component sorption systems was studied in fixed-bed column. The experiments were applied to quantify particle size, bed length, influent flow rate and influent metal concentration on breakthrough time during the removal of copper and lead ions from aqueous solutions using MOCZ column. Results of fixed-bed adsorption showed that the breakthrough time appeared to increase with increase of the bed length and decrease of influent metal concentration, but decreased with increase of the flow rate. The Thomas model was applied to adsorption of copper and lead ions at bed length, MOCZ particle size, different flow rate and different initial concentration to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. The model was found suitable for describing the adsorption process of the dynamic behavior of the MOCZ column. The total adsorbed quantities, equilibrium uptakes and total removal percents of Cu(II) and Pb(II) related to the effluent volumes were determined by evaluating the breakthrough curves obtained at different conditions. The results suggested that MOCZ could be used as an adsorbent for an efficient removal of copper and lead ions from aqueous solution. The removal of metal ion was decreased when other additional heavy metal ion was added, but the total saturation capacity of MOCZ for copper and lead ions was not significantly decreased. This competitive adsorption also showed that adsorption of lead ions was decreased insignificantly when copper ions was added to the influent, whereas a dramatic decrease was observed on the adsorption of copper ions by the presence of lead ions. The removal of copper and lead ion by MOCZ columns followed the descending order: Pb(II) > Cu(II). The adsorbed copper and lead ions were easily desorbed from MOCZ with 0.5 mol l⁻¹ HNO₃ solution.

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1. Introduction

The presence of heavy metals in the aquatic environment is a major concern due to their extreme toxicity towards aquatic life, human beings, and the environment. Although various treatment techniques have been employed to treat the wastewater, including chemical precipitation, ion exchange, filtration and adsorption on activated carbon, most of these methods suffer from some drawback such as ineffective, expensive, generation of secondary pollution and ineffectiveness for low metal con-

centration. Hence, there is a crucial need for the development of a method that is not only cost effective and economic, but can also be easily implemented. This led to a search for cheaper, easily obtainable materials for the adsorption of heavy metals.

Some natural materials such as zeolite, chitosan, clay may serve as cost-effective sorbents for the removal of heavy metals [1]. While their sorption capacity is usually less than those of synthetic or modified adsorbents, these minerals could provide inexpensive substitute for the treatment of heavy metal wastewaters. To enhance the sorption capacity of natural adsorbents towards heavy metals, many attempts have been made such as chemical modification of their surface using metal oxides [2–4]. Brandao and Galembeck reported that the impregnation of cellulose acetates with manganese dioxide resulted in high removal

* Corresponding author. Tel.: +86 371 67763707; fax: +86 371 67763220.
E-mail address: rphan67@zzu.edu.cn (R. Han).

efficiency of Cu(II), Pb(II), and Zn(II) from aqueous solutions [5]. Al-Degs and Khraishah [3] also reported that diatomite and manganese oxide modified diatomite are effective adsorbents for removing Pb^{2+} , Cu^{2+} , and Cd^{2+} ions. The sorption capacity of Mn-diatomite was considerably increased compared to the original material for removing the studied metals.

Zeolites are aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations (normally Na, K, Ca, and Mg) as well as water in their structural framework. The physical structure is porous, enclosing interconnected cavities in which the metal ions and water molecules are contained [6]. Zeolites represent an appropriate material for removing heavy metal ions from wastewater because of their relatively low price coupled with the fact that their exchangeable ions (Na^+ , Ca^{2+} , and K^+) are relatively harmless. Pretreatment of natural zeolites can improve the media performance, sorption capacity, increase mechanical strength, resistance to chemical environments and column operations.

Manganese oxides are typically thought to be the most important scavengers of aqueous trace metals in soil, sediments, and rocks through their seemingly dominant sorptive behavior. They have a large surface area, microporous structure, and high affinity for metal ions [7–10] (such as Pb, Cu, Cd, Zn and UO_2^{2+}), providing an efficient scavenging pathway for heavy metals in toxic systems. Commonly, the surface charge of manganese oxides is negative, and they can be used as adsorbents 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, 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.

The research described here was designed to test the properties of manganese oxide coated zeolite (MOCZ) as an adsorbent for removing copper and lead ions from synthetic solutions in fixed-bed column. Copper and lead ions were selected in this study as they are widely used in various industries and have negative effects on the aqueous environment. Specifically the paper investigates the effect of experimental conditions such as column length, particle size, flow rate, concentration of copper and lead ions, competitive effects between copper and lead ions on the sorption capability of MOCZ, and describes the kinetics of metal removal by the MOCZ adsorption column using the Thomas model.

The loading behavior of Cu(II) and Pb(II) to be removed from solution in a fixed-bed is usually expressed in term of C/C_0 (C = effluent metal ions concentration and C_0 = influent metal ions concentration) as a function of time or volume of the eluate for a given bed height, giving a breakthrough curve [11]. The maximum column capacity, q_{total} (mmol), for a given feed concentration and flow rate is equal to the area under the plot of the adsorbed Cu(II) and Pb(II) concentration C_{ad} ($C_{ad} = C_0 - C$) ($mmol\ l^{-1}$) versus time (min) and is calculated from Eq. (1):

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \quad (1)$$

where t_{total} , Q and A are the total flow time (min), volumetric flow rate ($ml\ min^{-1}$) and the area under the breakthrough curve, respectively.

The equilibrium uptake ($q_{eq(exp)}$), the weight of Cu(II) and Pb(II) adsorbed per unit dry weight of adsorbent ($mmol\ g^{-1}$) in the column, is calculated as following:

$$q_{eq(exp)} = \frac{q_{total}}{X} \quad (2)$$

where X is the total dry weight of MOCZ in column (g).

Total amount of Cu(II) and Pb(II) sent to column (W_{total}) is calculated from Eq. (3)

$$W_{total} = \frac{C_0 Q t_{total}}{1000} \quad (3)$$

Total removal percent of Cu(II) and Pb(II) is the ratio of the maximum capacity of the column (q_{total}) to the total amount of Cu(II) and Pb(II) sent to column (W_{total}).

$$Y = \left(\frac{q_{total}}{W_{total}} \right) \times 100 \quad (4)$$

Successful design of a column adsorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. The maximum adsorptive quantity of an adsorbent is needed in design. So various kinetics models have been developed to express the dynamic behavior of the column. The Thomas equation is one of the most general and widely used to predict the adsorption process [12]. It can be expressed as follows:

$$\frac{C}{C_0} = \frac{1}{1 + \exp[k_{Th}/Q(q_0 X - C_0 V_{eff})]} \quad (5)$$

where k_{Th} is the Thomas rate constant ($ml\ min^{-1}\ mmol^{-1}$); q_0 is the maximum solid-phase concentration of solute ($mmol\ g^{-1}$). X is amount of adsorbent in the column (g); V_{eff} is effluent volume (ml); C_0 is initial metal ions concentration ($mmol\ l^{-1}$); C is the effluent metal ions concentration ($mmol\ l^{-1}$); Q is flow rate ($ml\ min^{-1}$).

The linearized form of the Thomas model is as follows:

$$\ln \left(\frac{C_0}{C} - 1 \right) = \frac{k_{Th} q_0 X}{Q} - \frac{k_{Th} C_0}{Q} V_{eff} \quad (6)$$

The kinetic coefficient k_{Th} and the adsorption capacity of the column q_0 can be determined from a plot of $\ln(C_0/C - 1)$ against V_{eff} at a given flow rate.

2. Materials and methods

2.1. Adsorbent and adsorbates

The raw zeolite sample used in this study was obtained from Xinyang City in China. Before use, the zeolite was crushed and sieved through the mesh screens, and a fraction of average particle size was soaked in tap water for 24 h to decrease its alkaliessence, rinsed with distilled water and dried at 373 K in the oven in preparation for surface coating. Manganese oxide

coated zeolite 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 zeolite placed in a beaker, then hydrochloric acid (37.5%, $W_{\text{HCl}}/W_{\text{H}_2\text{O}}$) were 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 use.

Characterization of MOCZ and natural zeolite, such as SEM, surface area was compared by other paper [13]. The removal capacity of MOCZ was compared with that of raw zeolite in batch mode and the results showed that the MOCZ had bigger capacity of binding Cu(II) and Pb(II) than raw zeolite [13].

All chemicals and reagents used for experiments and analyses were of analytical grades. The chemicals used for the study were copper nitrate ($\text{Cu}(\text{NO}_3)_2$), lead nitrate ($\text{Pb}(\text{NO}_3)_2$), and nitric acid supplied by Shanghai Chemical reagent company (China). The solution of copper and lead were prepared by dissolving the salts in distilled water. The initial pH of the working solution was adjusted by addition of HNO_3 or NaOH solution.

2.2. Methods of adsorption studies

A series of experiments were conducted with various influent synthetic wastewater and MOCZ columns. The experiments involved three parts: adsorption of single-metal, competitive adsorption of dual-metal and desorption of metal ions in MOCZ column.

Fifteen gram MOCZ was packed into a glass column (1.0 cm inner diameter and 30 cm in height) with a bed depth of 15 cm. During the experiment of the effect by bed depth, the mass of MOCZ in the column was 5, 10, 15, and 20 g, respectively. Particle size of MOCZ packed in column was 20–40 mesh, except the experiment of the effect of particle size, the particle sizes of MOCZ in the column ranged from 16–20 mesh to 40–60 mesh. For single-component solutions, metal concentrations of copper ranged from 0.629 to 1.26 mmol l^{-1} and lead ranged from 0.955 to 1.54 mmol l^{-1} were used, respectively. For binary-component solution, the concentration of copper and lead ions was approximately 0.965 mmol l^{-1} . The initial pH was adjusted to 5.0 by addition of 0.1 mol l^{-1} HNO_3 or 0.1 mol l^{-1} NaOH solution. No other solutions were provided for additional ionic strength. Column experiments were conducted by pumping a metal solution in down flow mode through the fixed-bed with a peristaltic pump at a specified flow rate. The temperatures of all experiments were 293 K. Samples were collected at regular intervals and in all the adsorption and desorption experiments. The concentration of the free metal ions in the effluent was analyzed using flame atomic absorption spectrometer (AAS) (AAAnalyst 300, Perkin–Elmer). Upon column exhaustion, the adsorbed metals from MOCZ were eluted by using 0.5 mol l^{-1} HNO_3 solution. Usually, breakthrough and exhaustion were defined as the phenomenon when effluent concentrations were about 5% and 90%, respectively.

3. Result and discussion

3.1. Single-species metal ion adsorption

3.1.1. Effect of bed depth

The breakthrough curves of copper and lead ions adsorption obtained at different bed depths with a constant flow rate of 7.69 ml min^{-1} are given in Fig. 1(a) and (b), respectively. The bed depth of column on copper and lead ions sorption was packed to approximately 5, 10, 15, and 20 cm, corresponding to 5, 10, 15, and 20 g of MOCZ, respectively and the feed concentration with a synthetic solution contained copper ions (0.976 mmol l^{-1}) or lead ions (1.26 mmol l^{-1}), respectively.

The breakthrough curves in Fig. 1 showed that the breakthrough time and exhaustion time increased with the increase in bed depth and the slope of the plots from breakthrough time to exhaustion time decreased as the bed depth increased from 5 to 20 cm, indicating the breakthrough curve becomes steeper as the bed depth decreased. It is illustrated that the higher the bed depth the longer the service time at various breakthroughs due to the increase in binding sites on the adsorbent.

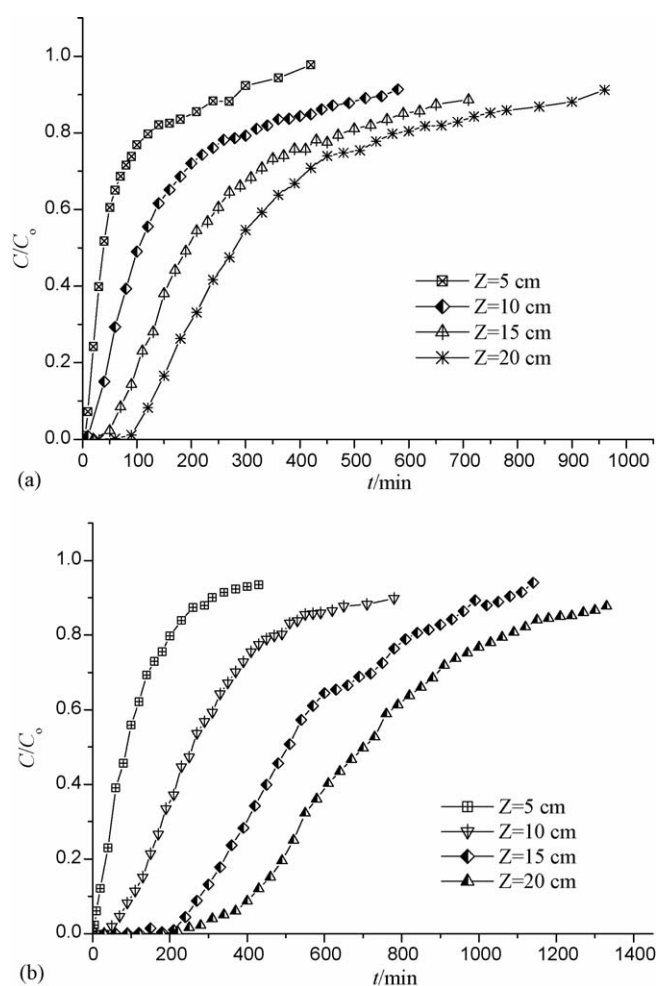


Fig. 1. Breakthrough curves of Cu(II) (a) and Pb(II) (b) for different bed depths and a flow rate of 7.69 ml min^{-1} and influent concentrations of copper 0.976 and lead 1.26 mmol l^{-1} , respectively.

Table 1

Parameters predicted from the Thomas model of copper and lead ions adsorption at different bed depth

Metal ion	Z (cm)	W_{total} (mmol)	q_{total} (mmol)	Y (%)	$q_{\text{eq(exp)}}$ (mmol g ⁻¹)	$q_{\text{o(cal)}}$ (mmol g ⁻¹)	k_{Th} (ml min ⁻¹ mmol ⁻¹)	R
Cu(II)	5	0.976	0.525	53.8	0.105	0.083	10.72	0.870
	10	2.252	1.201	53.3	0.120	0.092	7.46	0.915
	15	3.227	1.876	58.1	0.125	0.114	7.34	0.943
	20	4.503	2.702	60.0	0.135	0.125	4.62	0.920
Pb(II)	5	2.229	1.211	54.3	0.242	0.231	8.79	0.929
	10	4.942	2.907	58.8	0.291	0.281	5.78	0.966
	15	8.139	5.281	64.9	0.352	0.346	5.39	0.980
	20	10.85	7.267	67.0	0.363	0.365	3.51	0.970

3.1.2. Application of Thomas model

To determine the maximum solid-phase concentration (q_0) at different bed depth in column, the data were fitted to the Thomas equation model by using linear regression analysis. A plot of $\ln(C_0/C - 1)$ versus V gives a straight line with a slope of $(-k_{\text{Th}}C_0/Q)$ and an intercept of $(k_{\text{Th}}q_0X/Q)$. Therefore, the values of equation parameters such as k_{Th} and q_0 which application of Thomas model to the data at C/C_0 ratios higher than 0.05 and lower than 0.90 with respect to different flow rate can be obtained. The relative parameters were listed in Table 1.

As shown in Table 1, the removal efficiency of Cu(II) and Pb(II) increase with an increase in bed height, and results also showed bigger equilibrium capacities ($q_{\text{eq(exp)}}$) of the four bed heights with values from 0.105 and 0.242 mmol g⁻¹ to 0.135 and 0.363 mmol g⁻¹ for Cu(II) and Pb(II), respectively. The increase in the metal uptake capacity with the increase of bed heights in the column was due to the increase in the surface area of adsorbent that provided more binding site for the adsorption. From Table 1, it also can be seen that the values of k_{Th} decrease with increasing of the bed height. Inspection of each lines indicated that they were all fit with linear regressive coefficients ranging from 0.915 to 0.980, except the line obtained from the 5 cm bed height of copper removal. With the higher value of R, it can be said that the Thomas model equations of linear regression analysis could describe the breakthrough data in the studied conditions. The maximum adsorption capacities ($q_{\text{o(cal)}}$) of Cu(II) and Pb(II) on MOCZ predicted by the model were found to be affected by bed depth, and the values of $q_{\text{o(cal)}}$ estimated by this model differed insignificant of those measured experimentally. So it is indicated that the Thomas model gave a well fit of experimental data at this studied conditions.

3.1.3. Effect of flow rate

To investigate the effect of flow rate on Cu(II) and Pb(II) by MOCZ, the inlet metal concentration in the feed was held constant at 0.976 mmol l⁻¹ (for copper) and 1.26 mmol l⁻¹ (for lead), respectively. The flow rate was from 5.45 to 10.0 ml min⁻¹ at a bed depth of 15 cm. The plots of the ratio of effluent to influent metal ion concentrations versus time for the adsorption of Cu(II) and Pb(II) and effluent pH versus time are present in Fig. 2 (a) and (b).

It is illustrated that the breakthrough time reaching saturation was increased significantly with a decreased from 10.0 to 5.45 ml min⁻¹ and the breakthrough curves shifted from left to

right. This is because the time required to reach an equilibrium state between MOCZ and heavy metal solutions is approximately 3 h (according to the batch experiments) [13]. Therefore, increasing the flow rate causes a shorter retention time, and the supply speed of metal ions to column decreases, so the breakthrough curves shifted from left to right.

From Fig. 2 it displays two important features: rapidly decreased of the effluent pH at the beginning of column operation, and an eventual period of slowly increased concentration of copper and lead ions in effluent level. A dramatic change in the effluent pH was observed in this study, as shown in Fig. 2. Efflu-

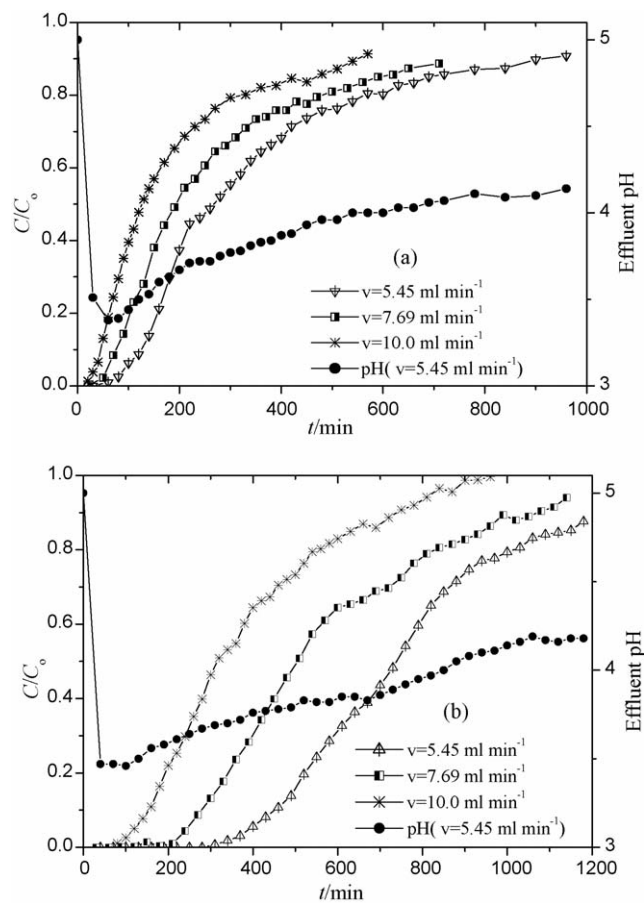


Fig. 2. Breakthrough curves of Cu(II) (a) and Pb(II) (b) for different flow rates and a bed depth of 15 cm and influent concentrations of 0.976 and 1.26 mmol l⁻¹ of Cu(II) and Pb(II), respectively.

Table 2
Parameters predicted from the Thomas model of copper and lead ions adsorption at different flow rates

Metal ion	Q (ml min ⁻¹)	W_{total} (mmol)	q_{total} (mmol)	Y (%)	$q_{\text{eq(exp)}}$ (mmol g ⁻¹)	$q_{\text{o(cal)}}$ (mmol g ⁻¹)	k_{Th} (ml min ⁻¹ mmol ⁻¹)	R
Cu(II)	5.45	3.351	1.968	58.7	0.131	0.119	5.01	0.908
	7.69	3.227	1.876	58.1	0.125	0.114	7.34	0.943
	10.0	2.928	1.659	56.5	0.111	0.104	12.2	0.922
Pb(II)	5.45	7.897	5.391	68.3	0.359	0.355	5.21	0.970
	7.69	7.848	5.087	64.8	0.339	0.346	5.39	0.980
	10.0	7.560	4.662	61.7	0.310	0.312	5.98	0.962

ent pH was drop from 5.0 of the influent solution to 3.4 rapidly at the beginning of column operation first, and then elevated slowly to approximately 4.3 at the exhausting point. As the initial rate of adsorption is faster, the amount of binding metals onto MOCZ is more, more hydrogen ions were released into solution as ion exchange or surface complexation process, so the value of pH decreased rapidly at the initial process. Besides, it is clear that an approximately constant removal of Cu(II) and Pb(II) is maintained over a long period after breakpoint and only a minor portion of influent copper and lead ions could be adsorbed by other unoccupied sites. It is attributed to a very slow diffusion of the adsorbed metals from the surface film into the micropores that are the least accessible sites of adsorption [14].

The uptake capacity of Cu(II) and Pb(II) was decreased with the increase of flow rate in the column and the removal efficiency of Cu(II) and Pb(II) was also decrease with an increase in flow rate as shown in Table 2. At low flow rates, sorption of both Cu(II) and Pb(II) increased due to the long retention time in the column, which resulted in higher removal of metal ions in fixed-bed column. According to linearized Thomas equation (Eq. (6)), the k_{Th} , q_{o} and regression coefficients R were calculated and are shown in Table 2. The adsorption capacity ($q_{\text{eq(exp)}}$) of copper and lead ions on MOCZ decreased from 0.131 to 0.111 mmol g⁻¹ and 0.359 to 0.310 mmol g⁻¹, respectively with increasing flow rate from 5.45 to 10.0 ml min⁻¹. With the flow rate increasing, the value of k_{Th} increased with the same inlet concentration. Inspection of each lines indicated that they were all fits with linear coefficients ranging from 0.943 to 0.980, except the line obtained from the flow rate was 5.45 and 10.0 ml min⁻¹ of copper. The calculated $q_{\text{o(cal)}}$ values also agree well with the experimental data ($q_{\text{eq(exp)}}$). With the higher value of R , it can be said that the Thomas model equations of linear regression analysis could describe the breakthrough data in the studied concentration range.

3.1.4. The effect of initial concentration of metal ions

The effect of initial influent concentration was investigated using synthetic solution containing 0.629, 0.976, 1.26 mmol l⁻¹ of copper and 0.955, 1.26, 1.54 mmol l⁻¹ of lead ions, respectively. From Fig. 3, it shows the effect of initial concentration on the breakthrough curves by using a bed depth of 15 cm at a flow rate of 7.69 ml min⁻¹. As shown from the breakthrough curves in Fig. 3, breakthrough ($C/C_0 = 0.05$) occurred after 60 min and 160 min at inlet concentration of copper 1.26 mmol l⁻¹ and lead 1.54 mmol l⁻¹, respectively, which as the breakpoint time appeared after 100 and 220 min at an inlet concentration of cop-

per 0.629 mmol l⁻¹ and lead 0.955 mmol l⁻¹, respectively. It is illustrated that the breakthrough time decreased with increasing influent metal ion concentration. At lower influent metal ion concentrations, breakthrough curves were dispersed and breakthrough occurred slower. As influent concentration increased, sharper breakthrough curves were obtained. Comparing the case for lead ion adsorption with that of copper ions adsorption, it was found that the normalized effluent concentration curves for copper ions adsorption were steeper.

As shown in Table 3, the copper and lead ions adsorption characteristics were dependent on initial concentration. The adsorption capacity ($q_{\text{eq(exp)}}$) of Cu(II) and Pb(II) was increased from

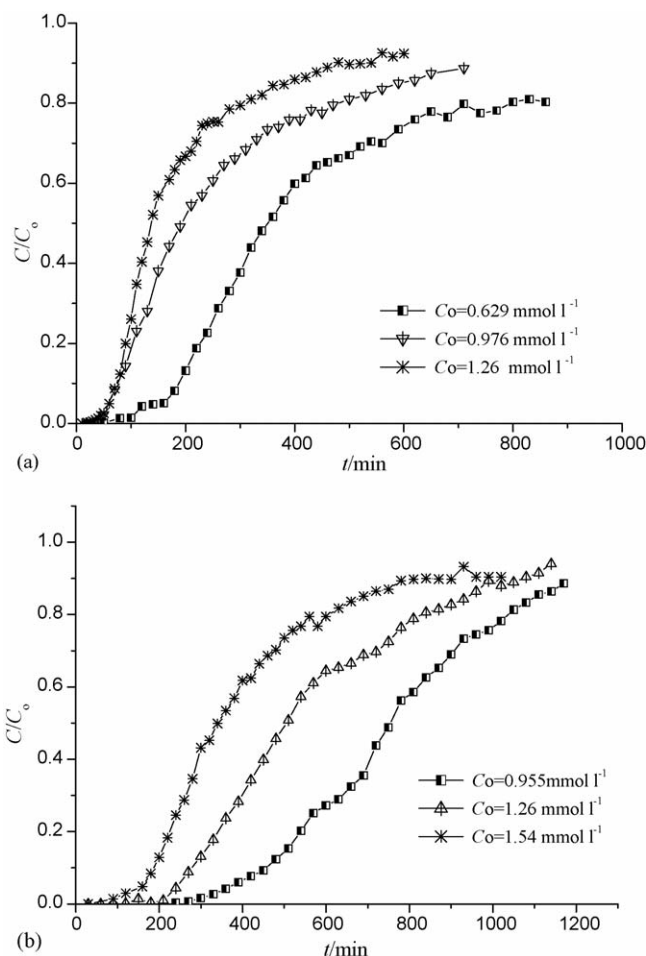


Fig. 3. Breakthrough curves of Cu(II) (a) and Pb(II) (b) for different influent concentrations at a bed depth of 15 cm and flow rate of 7.69 ml min⁻¹.

Table 3

Parameters predicted from the Thomas model of copper and lead ions adsorption at different initial metal concentrations

Metal ion	C_0 (mmol l ⁻¹)	W_{total} (mmol)	q_{total} (mmol)	Y (%)	$q_{\text{eq(exp)}}$ (mmol g ⁻¹)	$q_{\text{o(cal)}}$ (mmol g ⁻¹)	k_{Th} (ml min ⁻¹ mmol ⁻¹)	R
Cu(II)	0.629	3.096	1.838	59.4	0.123	0.106	5.25	0.937
	0.976	3.227	1.876	58.1	0.125	0.114	7.34	0.943
	1.26	3.391	1.986	58.6	0.132	0.116	6.02	0.888
Pb(II)	0.955	7.491	4.957	66.2	0.330	0.339	6.02	0.993
	1.26	7.848	5.087	64.8	0.339	0.346	5.39	0.980
	1.54	8.171	5.151	63.0	0.343	0.349	3.80	0.909

0.123 and 0.330 mmol g⁻¹ to 0.132 and 0.343 mmol g⁻¹ with increasing of initial metal concentration, while the removal percent of Cu(II) and Pb(II) decreased. The column data for Cu(II) and Pb(II) was fitted to the linearized form of the Thomas model at different metal concentrations. From linearized Thomas equation plots, the k_{Th} , q_0 and regression coefficients R were calculated and are listed in Table 3. The maximum adsorption capacities ($q_{\text{o(cal)}}$) of Cu(II) and Pb(II) on MOCZ predicted by the model, were found to be affected by initial metal concentrations. The values of $q_{\text{o(cal)}}$ increased from 0.106 to 0.116 mmol g⁻¹ and 0.339 to 0.349 mmol g⁻¹ as the initial metal concentrations of copper and lead ions changed from 0.629 to 1.26 mmol l⁻¹ and 0.955 to 1.54 mmol l⁻¹, respectively. This can be explained by the fact that more adsorption sites are being covered as the adsorbate concentration increases. Due to the higher initial metal concentration gradient, the mass transfer driving force will be higher [15]. In view of the values of linear regression coefficients, the Thomas model fitted well to the sorption data in the studied concentration range. The values of $q_{\text{o(cal)}}$ obtained from the Thomas equation for lead adsorption on MOCZ appeared almost three-fold greater to that of copper, which is indicated that the functional groups on the surface of MOCZ had a relatively stronger affinity for lead ions than copper ions and potential of the adsorption for copper and lead ions on MOCZ was in the following order: lead > copper.

3.1.5. The effect of particle size

The adsorption process of MOCZ was performed at various particle sizes. Fig. 4 showed the results of the experiments carried out at a flow rate of 7.69 ml min⁻¹ for different particle sizes ranged from 16–20 mesh to 40–60 mesh. The initial concentrations of a synthetic solution were 0.976 mmol l⁻¹ for copper and 1.26 mmol l⁻¹ for lead, respectively.

From Fig. 4, it was shown breakthrough ($C/C_0 = 0.05$) of Cu(II) and Pb(II) occurred after 30 min and 40 min at particle size of 16–20 mesh, respectively, which as breakpoint time appeared after 70 min and 320 min at particle size of 40–60 mesh, respectively. The breakthrough curve of the smaller particle size raised a little steeply ranged from the breakpoint to the exhaustion point. The adsorption capacity of Pb(II) decreased with increasing adsorbent particle size. But the particle size effect is minimal for Cu(II). This result is in agreement with that reported by Ören and Kaya's studies [16]. From Table 4, it also can be seen that with the particle size decreasing, the values of k_{Th} increase with the same inlet concentration. The maximum adsorption capacities ($q_{\text{o(cal)}}$) estimated by Thomas model differed insignificant

of those measured experimental data, so the Thomas model can give a well fit of experimental data at this studied conditions.

3.2. The competitive adsorption of copper and lead ions

In order to investigate the effect of coexistence ions on the adsorption of MOCZ, adsorption experiments for binary-component metal ions (Cu–Pb) with influent pH 5.0 under identical conditions were conducted with MOCZ columns. The experiments of competitive adsorption of Cu(II) and Pb(II) included three parts: Cu(II) and Pb(II) were adsorbed simultaneously;

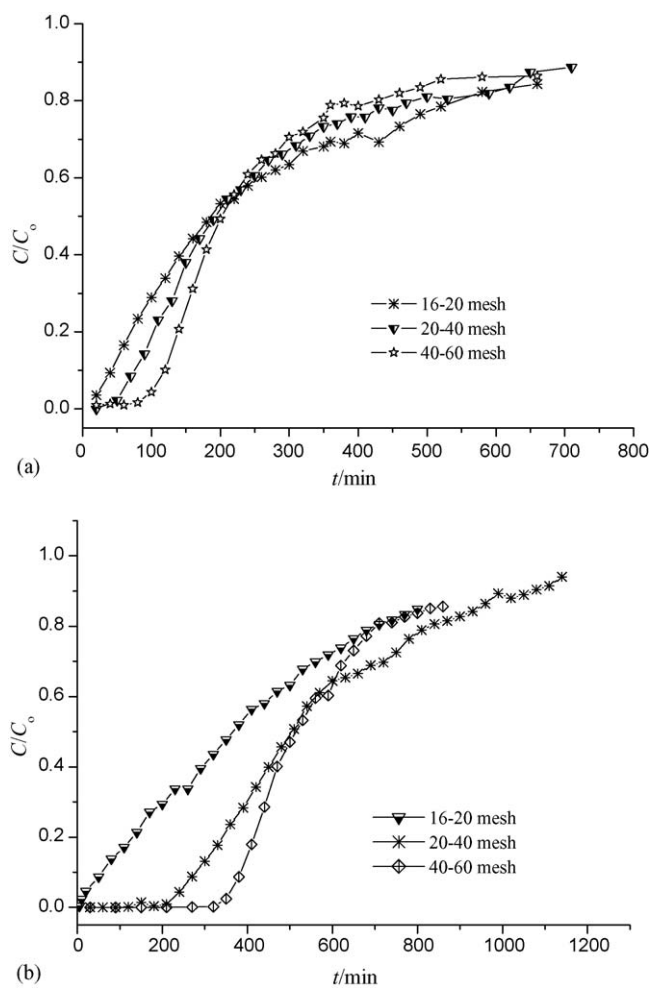


Fig. 4. Breakthrough curves of Cu(II) (a) and Pb(II) (b) for different particle sizes at a bed depth of 15 cm, flow rate of 7.69 ml min⁻¹ and influent concentrations of Cu(II) 0.976 mmol l⁻¹ and Pb(II) 1.26 mmol l⁻¹, respectively.

Table 4
Parameters predicted from the Thomas model of copper and lead ions adsorption at different particle sizes

Metal ion	Particle size (mesh)	W_{total} (mmol)	q_{total} (mmol)	Y (%)	$q_{\text{eq(exp)}}$ (mmol g ⁻¹)	$q_{\text{o(cal)}}$ (mmol g ⁻¹)	k_{Th} (ml min ⁻¹ mmol ⁻¹)	R
Cu(II)	16–20	3.903	1.838	47.1	0.123	0.109	4.71	0.960
	20–40	3.227	1.876	58.1	0.125	0.114	7.34	0.943
	40–60	3.077	1.951	63.4	0.130	0.119	9.30	0.909
Pb(II)	16–20	7.170	3.730	52.0	0.249	0.259	3.91	0.987
	20–40	7.848	5.087	64.8	0.339	0.346	5.39	0.980
	40–60	6.879	5.232	76.1	0.349	0.358	6.08	0.949

after Cu(II) saturation, Pb(II) was adsorbed; after lead ions saturation, then copper ions was adsorbed.

3.2.1. The simultaneous adsorption of copper and lead ions from binary metal mixtures by MOCZ column

A solution containing Cu(II) and Pb(II) was used in the study, with a concentration of approximately 0.965 mmol l⁻¹ for each ion, which was the approximate concentration used for the tests with single-component solutions.

This competitive adsorption showed that adsorption of lead ions was slightly reduced with the presence of copper in the influent solution, however the competitive on copper ions adsorption by lead ions was quite significant as shown in Fig. 5. It is illustrated that MOCZ was less favorable for copper ions, lead ions competed adsorption sites with copper ions and the adsorption of copper ions was decreased as lead ions added. Hence, the breakthrough for copper ions adsorption occurred immediately after the experiments were started. At the run progressed and the available sites for binding copper were saturated, however, lead ions not only reacted with the remaining sites, but also displace a portion of the weakly bound copper ions, so the effluent concentration of copper was greater than the influent. This also indicated that the function groups on the surface of MOCZ had a relatively stronger affinity for lead ions than copper ions.

Values of the column uptake capacities $q_{\text{o(cal)}}$ obtained from the Thomas model for the binary-component system at described conditions were 0.029 and 0.296 mmol g⁻¹ for copper and lead

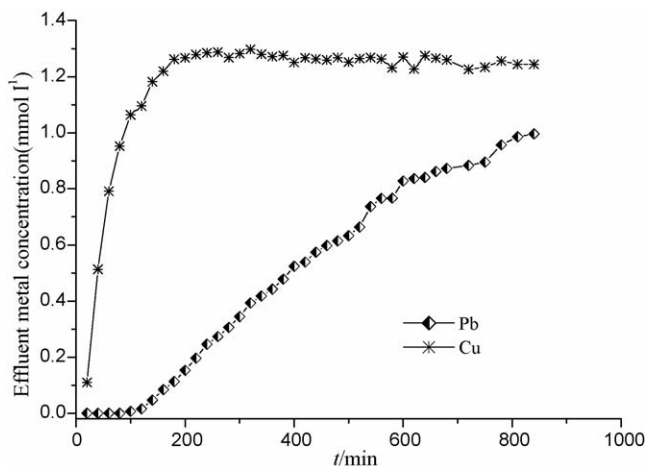


Fig. 5. Breakthrough curves of Cu(II) and Pb(II) adsorbed simultaneously on MOCZ at a bed depth of 15 cm and flow rate of 7.69 ml min⁻¹.

ions, respectively, which were less than those for the single-component solutions. However, the total adsorption capacity for these two metals exceeded the capacity than that of copper but less than that of lead 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.

3.2.2. The MOCZ column saturated by copper(II), then lead(II) solution passed through

In this experiment, we studied the effect of lead ions to adsorbed copper ions on MOCZ. Firstly, the column of MOCZ at a bed depth of 15 cm was saturation by feed a single-component solution containing of copper 0.965 mmol l⁻¹, then a single-component solution containing of 0.965 mmol l⁻¹ lead applied in this experiment, was passed through the column at a flow rate of 7.69 ml min⁻¹. The breakthrough curve was shown in Fig. 6. It was plotted as the point of effluent concentrations of copper and lead ions versus time. As shown in Fig. 6, effluent concentration of copper elevated rapidly from 0 of the influent solution to 0.82 mmol l⁻¹ at the beginning of column operation, then drop slowly to near zero at the exhausting point, while the concentration of lead was not detected at the beginning of experiment and finally a period of slow increase in initial level. It is concluded that copper adsorbed on MOCZ can be easily replaced by lead and eluted from the column. This is because that the function groups on the surface of MOCZ had a relatively stronger affinity for lead ions than copper ions. Lead ions can compete with copper to bind the adsorbing sites existed on the MOCZ. Hence,

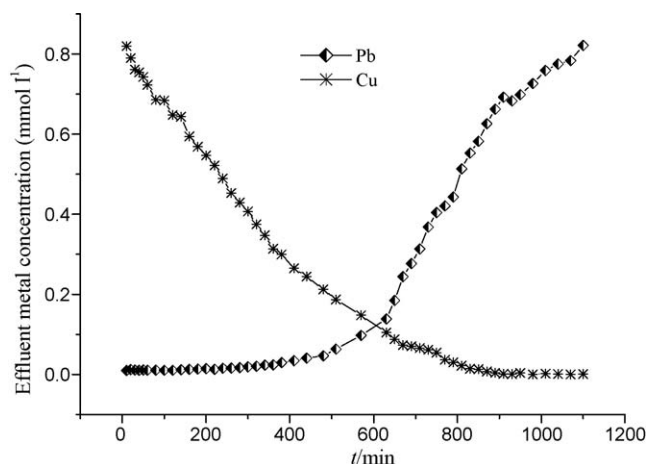


Fig. 6. Copper ions replaced by lead ions from adsorbed-copper MOCZ.

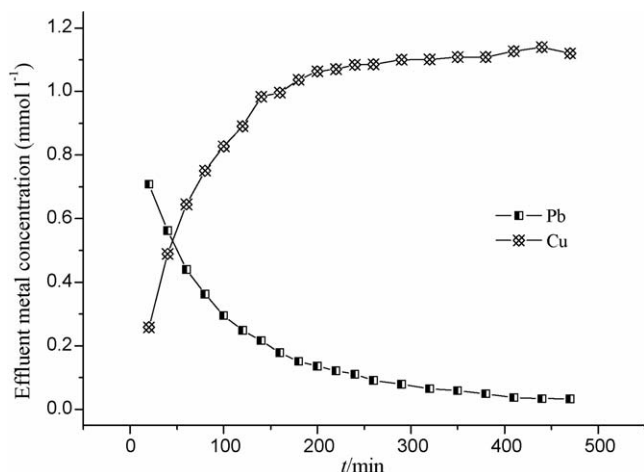


Fig. 7. Lead ions replaced by copper ions from adsorbed-lead MOCZ.

copper ions that have been adsorbed on the active sites were easily replaced by lead ions, and re-existed in solution.

3.2.3. The MOCZ column saturated by lead(II), then copper(II) solution passed through

This experiment was investigated the effect of additional copper ions to adsorbed lead ions on MOCZ. Firstly, the column of MOCZ at a bed depth of 15 cm was saturation by feed a single-component solution containing of lead $0.965 \text{ mmol l}^{-1}$, then a single-component solution containing of copper $0.965 \text{ mmol l}^{-1}$ applied in this experiment, was passed through the column at a flow rate of 7.69 ml min^{-1} . The breakthrough curve was shown in Fig. 7. The most favorable metal ion, Pb, occupied almost all the adsorption sites on the adsorption sites of MOCZ column, thus less favorably adsorbed metal ions, Cu, breakthrough more rapidly. As shown in Fig. 7, much shaper breakthrough curve of copper was obtained by MOCZ while the influent copper solution was fed the column.

From the studies of the competitive adsorption of copper(II) and lead(II) onto MOCZ in fixed-bed columns, it can be concluded that adsorption of metal ions was generally decreased with the presence of other metals in the influent solution. As MOCZ was favorable for lead ions as shown in Fig. 5, the competition caused by addition of copper ions was insignificant, while the competition on copper ions adsorption by lead ions was quite significant. Therefore, addition of stronger binding metal ions, such as lead, could weaken the chemical bonds between the functional group on the surface of MOCZ and weaker metal ions, such as copper ions. The adsorption order for copper and lead ions in the binary-component system is $\text{Pb(II)} > \text{Cu(II)}$. This observation is in agreement with that reported by other studies [17].

3.3. Desorption

Once the column reached exhaustion, it is important to regenerate MOCZ for the recovery of metal ions as well as the reuse of MOCZ for adsorption. Desorption of metals was investigated using $0.5 \text{ mol l}^{-1} \text{ HNO}_3$ solution as the desorbed agent at the

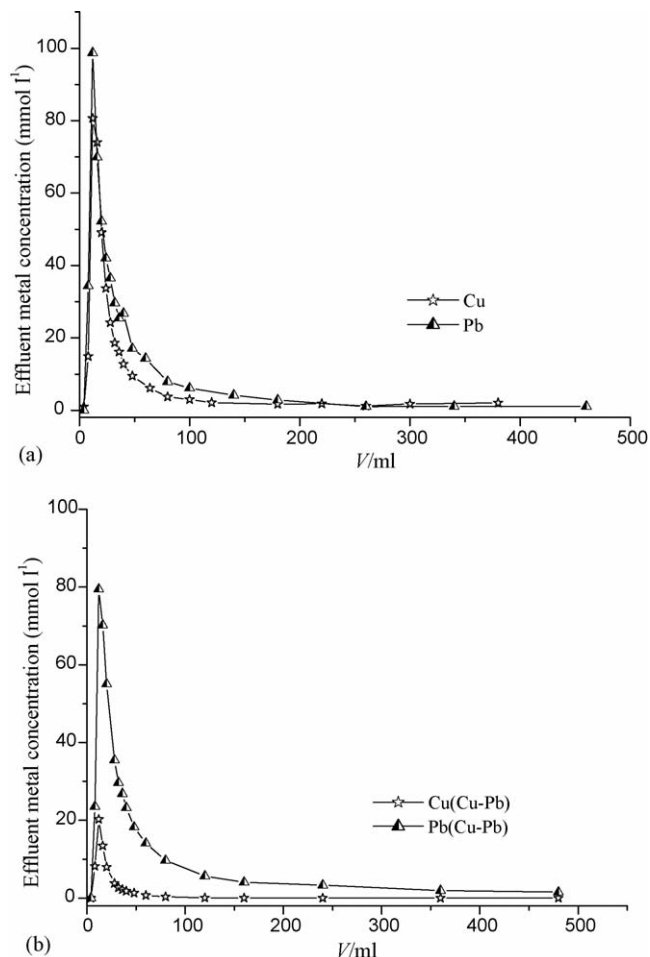


Fig. 8. Elution curves for copper and lead ions from MOCZ column using $0.5 \text{ mol l}^{-1} \text{ HNO}_3$ solution at flow rate of 4 ml min^{-1} (a) single-component system; (b) binary-component system.

flow rate of 4 ml min^{-1} in the same column, respectively. The concentrations of metal ions in eluants for columns that had been fed with single-component and binary-component solution are shown in Fig. 8(a) and (b), respectively.

The result exhibit a sharp increase of Cu^{2+} and Pb^{2+} concentration at the beginning of acid elution, with the maximum concentration of copper 80.6 and lead 98.7 mmol l^{-1} , which was 83-fold and 78-fold the feeding copper and lead concentration in the adsorption operation as shown in Fig. 8(a). The majority of the adsorbed copper and lead ions from the column were eluted in approximately 50 and 70 ml HNO_3 solution in single-component system, respectively. The majority of the adsorbed copper and lead ions from the column were eluted in approximately 20 and 80 ml, $0.5 \text{ mol l}^{-1} \text{ HNO}_3$ solution, respectively, in binary-component solution as shown in Fig. 8(b). The maximum concentration of copper and lead were 20 and 79.4 mmol l^{-1} , which were less than those for the single-component system. The reason is that the values of the column uptake capacities $q_{\text{eq}(\text{exp})}$ for copper or lead ions in the binary-component system were less than those in the single-component solutions. These data showed that more than 99% of adsorbed metal can be easily eluted from the column.

4. Conclusion

On the base of the experimental results of this investigation, the following conclusion can be drawn:

- (1) MOCZ was found to be an effective adsorbent for removal of copper and lead ions.
- (2) The Thomas mathematical model adequately described the adsorption of copper and lead ions onto MOCZ by column mode.
- (3) The removal efficiency of metal ions was decreased when other heavy metal ion existed, and MOCZ had a relatively stronger affinity for lead ions than copper ions.
- (4) Copper and lead ions are both easily desorbed from the MOCZ column using HNO₃ solution.

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