

Biosorption of copper(II) and lead(II) from aqueous solution by chaff in a fixed-bed column

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Received 2 September 2005; received in revised form 5 October 2005; accepted 12 October 2005

Available online 17 November 2005

Abstract

In this article, the ability of chaff to adsorb heavy metal ions from aqueous solution was investigated in a fixed-bed column. The effect of important parameters, such as the value of pH, the flow rate, the influent concentration of solution and the effect of coexistence ions, was studied. Also the adsorption/desorption recycles of chaff were shown, and the results indicated that chaff could be recycled to remove heavy metal ions. The Thomas model was applied to adsorption of copper and lead at different flow rate and different influent 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 biosorption process of the dynamic behavior of the chaff column. All the results suggested that chaff as adsorbent to removal heavy metal ions from solution prove efficient, and the rate of biosorption process is speedy. Furthermore, the efficiency of adsorption is high. When the flow rate was 3.6 ml min^{-1} and the influent concentration of copper and lead was 14.82 mg l^{-1} and 50.12 mg l^{-1} respectively, the equilibrium adsorption biomass reached 1.98 mg g^{-1} and 6.72 mg g^{-1} , respectively. The competitive adsorption for lead and copper was studied. Moreover the total adsorbing capability of chaff did not decrease when there were both copper(II) and lead(II) in solution.

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Keywords: Biosorption; Chaff; Copper cation; Lead cation; Competitive adsorption

1. Introduction

The removal of heavy metals ions from wastewater has received a great attention in recent decade years for global awareness of the underlying detriment of heavy metals in the environment. Application traditional treatment techniques need enormous cost and continuous input of chemicals, which become impracticable and uneconomical and cause further environment damage. Hence, easy, effective, economic and eco-friendly techniques are required for fine tuning of effluent wastewater treatment.

The search for a low cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin, along with industrial by-products, as adsorbents [1,2]. The living microorganisms cannot exchange heavy metals as they should be metabolically inactive. Generally, the dead

biomass is used as biosorbent [3–5]. The biosorption technology and its potential for the treatment of wastewater and environmental pollution have been recently outlined [6–8]. The sorption capacity parameter obtained from a batch experiment is useful in providing information about effectiveness of metal-biosorbent system. However, the data obtained under batch conditions are generally not applicable to most treatment system (such as column operations) where contact time is not sufficient long for the attainment of equilibrium. Hence, there is a need to perform equilibrium studies using columns.

Rice husk or bran has been used to removal heavy metals from aqueous solution [9,10]. But in this paper, corn chaff was chosen as biosorbent. Firstly, it contains abundant floristic fiber, protein and some functional groups, such as carboxyl, hydroxy and amidogen, etc., which make adsorption processes possible [11]. Secondly, the adsorbent of chaff obtained from agriculture as a by-product, furthermore their yield is vastness. Usually, chaff was as feed to raise livestock and poultry and did not have any extensive use. Harvesting in Henan, Hebie and Shanxi in China, the chaff is not only abundant but also cost cheap. Biosorption for lead(II) from aqueous solution by chaff in batch mode has been studied and the chaff can be as a adsorbent to

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bind lead [12]. The aim of this study is to develop a new and cheap technology for the removal of heavy-metals pollutions from wastewater and other aqueous system. The objectives of present work were to investigate effects of flow rate, the pH value, competitive metal ions, influent concentration and other factors on metal removal by chaff. Copper(II) and lead(II) were selected in this study as they are widely used in various industries and have negative effects on the water environment.

2. Materials and methods

2.1. Preparation of biomass

Fresh biomass of chaff was collected from its natural habitats on the dead millet in the farmland, Luoyang City, China. It was washed a few times with distilled water, dried for 8 h at 60 °C in the oven. The biomass was sieved and a fraction of average particle size (0.5 mm) was used for equilibrium and column studies. The chaff are mainly composed by carbohydrates, lignin, cellulose and no volatile substance is only 11% in the total weight [11].

2.2. Metal solution

The chemicals used for the study were analytical grades of lead nitrate ($\text{Pb}(\text{NO}_3)_2$), copper nitrate ($\text{Cu}(\text{NO}_3)_2$) and nitric acid supplied by Luoyang Chemical reagent company (China). The stock solution (1000 mg l^{-1}) of copper and lead were prepared by dissolving them in distilled water.

2.3. Methods of adsorption studies

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

Chaff was packed into a glass column (1.5 cm in diameter and 30 cm in height). Except the experiment of the effect of pH values, the mass of chaff in the column was 4.24 g and the value of pH was 5.0. The metal solution containing copper and lead at different concentration were applied to the column. The pH of metal solution was adjusted by adding 0.1 mol l^{-1} nitric acid solution. No other solutions to provide additional ionic strength. The metal solution was pumped to the column in a down-flow direction by a peristaltic pump at a certain rate. 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) (AAAnalyst300, Perkin-Elmer). The concentration of metal ions desorbed from chaff column by 0.1 mol l^{-1} nitric acid solution also was analyzed.

2.4. Thomas model

The data obtained in column in continuous mode studies was used to calculate maximum solid phase concentration of metals

on biosorbent and the adsorption rate constant using the kinetic model developed by Thomas [13]. The Thomas solution is one of the most general and widely used methods in column performance theory. The expression by Thomas for an adsorption column is given as follows:

$$\frac{c_t}{c_0} = \frac{1}{1 + \exp[k_{\text{Th}}(q_0x - c_0V_{\text{eff}})/v]} \quad (1)$$

where k_{Th} is the Thomas rate constant ($\text{ml min}^{-1} \text{ mg}^{-1}$), q_0 the equilibrium metal uptake per gram of the adsorbent (mg g^{-1}), x the amount of adsorbent in the column (g), V_{eff} the effluent volume (ml), c_0 the influent metal ion concentration (mg l^{-1}), c_t the effluent concentration at time t (mg l^{-1}) and v the flow rate (ml min^{-1}). The value of c_t/c_0 is the ratio of effluent and influent metal concentrations. The value of t is time (min, $t = V_{\text{eff}}/v$).

The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{c_0}{c_t} - 1\right) = \frac{k_{\text{Th}}q_0x}{v} - \frac{k_{\text{Th}}c_0V_{\text{eff}}}{v} \quad (2)$$

The kinetic coefficient k_{Th} and the adsorption capacity of the column q_0 can be determined from a plot of $\ln\left(\frac{c_0}{c_t} - 1\right)$ against V_{eff} (or t) at a given flow rate [3].

3. Result and discussion

3.1. The effect of initial pH

In order to examine the pH variation as well as its effect on metal ions biosorption in columns, single-species metal ion adsorption experiments were done. Fig. 1 shows the effect of pH values on adsorption of copper(II) (a) and lead(II) (b) onto chaff using a plot of dimensionless concentration (c_t/c_0) versus time (t). The influent concentration of copper was all 7.44 mg l^{-1} , the mass of chaff in the column was 2.24 g, value of pH was 3.0, 4.0 and 5.0, respectively. The flow rate was all 7.5 ml min^{-1} . The influent concentration of lead was all 25.2 mg l^{-1} . Other factors are same to copper.

From Fig. 1a, it was shown that when the value of pH was 3.0, the value of c_t/c_0 reached 0.9 in 20 min for copper, while the breakthrough curve of the pH equal 5.0 was not more than 0.8 in the same time. Similar results were observed from Fig. 1b. Obviously, with an increase of pH in the influent, the breakthrough curves shifted from left to right, which indicates that more metal ions can be removed. It would spend more time reaching the saturation, and the efficiency of biosorption was much higher. The results suggested that with the increasing of pH, the adsorption capacities increase. So the removal of copper and lead from aqueous solution was more efficient.

The values of pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the biosorption availability of the heavy metals. At low pH value, the surface of adsorbent would also be surrounded by hydronium ions, which

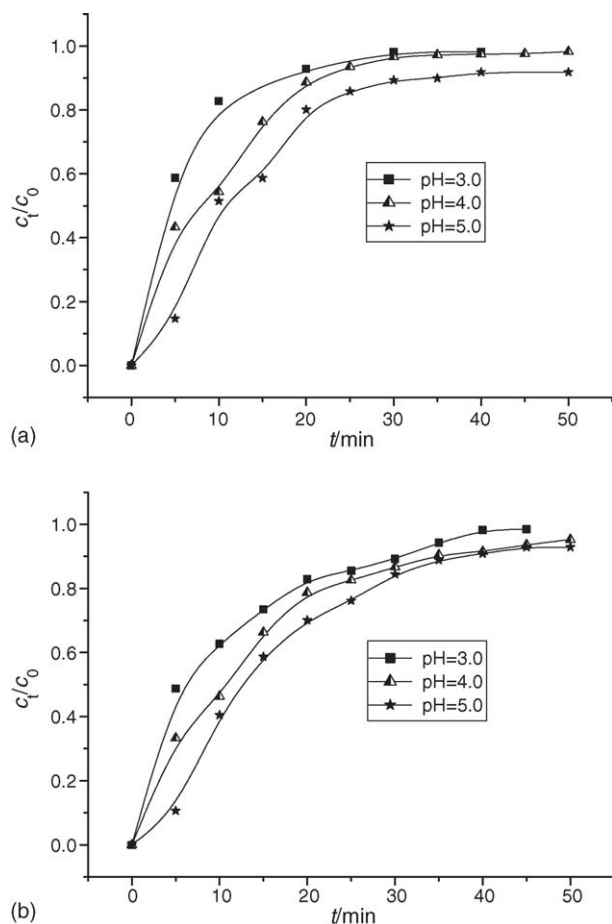


Fig. 1. The effect of pH values on biosorption of copper(II) (a) and lead(II) (b) by chaff ($v = 7.5 \text{ ml min}^{-1}$, $c_{0-\text{Cu}} = 7.44 \text{ mg l}^{-1}$, $c_{0-\text{Pb}} = 25.2 \text{ mg l}^{-1}$).

decrease the copper and lead interaction with binding sites of the chaff by greater repulsive forces. Even at pH 2.0 values, there were still biosorption capacity, this indicated that the mechanism of biosorption is not only ion-exchange, there should be other mechanism in the process of metal ions biosorption on biosorbent [10,12]. As the pH increased, the overall surface on the chaff became negative and adsorption increased. However, when pH values increase to 6.5, there is possibility of some precipitation of insoluble copper and lead hydroxide on the adsorbent surface in the bed, making true sorption studies impossible, both adsorption and precipitation are the effective mechanisms to remove the copper(II) and lead(II) in aqueous solution. Similar studies were found by other authors [14,15].

3.2. The effect of flow rate

To investigate the effect of flow rate on the single-component biosorption of copper(II) and lead(II) by chaff, the influent metal concentration was held constant at 14.8 mg l^{-1} and 50.1 mg l^{-1} , respectively, and the flow rate was changed from 3.6 ml min^{-1} to 8.3 ml min^{-1} . The breakthrough curve shown in Fig. 2 was a plot of dimensionless concentration (c_t/c_0) versus time (t). It was shown that breakthrough generally occurred faster with faster flow rate. Breakthrough time reaching saturation was increased

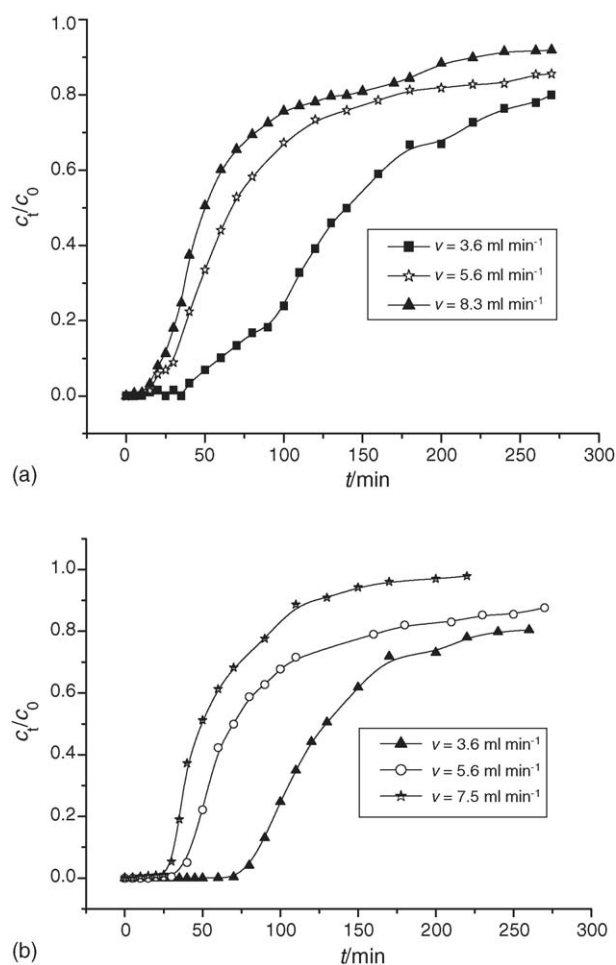


Fig. 2. The effect of flow rate of copper(II) (a) and lead(II) (b) on biosorption by chaff ($c_{0-\text{Cu}} = 14.8 \text{ mg l}^{-1}$, $c_{0-\text{Pb}} = 50.1 \text{ mg l}^{-1}$).

significantly with a decreased in the flow rate. In the foremost interval, the value of c_t/c_0 increased quickly since it has reached 0.8, the change then became slowly. When at a low rate of influent, metal ions had more time to contact with chaff that resulted in higher removal of metal ions in column. While increasing the flow rate, the results indicated that the adsorption capacity would reach the equilibrium value faster, which may cause a negative effect on the mass transferring efficiency of the metal ions. From the two figures it was observed that there were very similar effects on biosorption of copper and lead onto chaff in column. The difference was that the breakthrough time is shorter at the same c_t/c_0 (smaller than 0.1). Thus, it is possible to choose an appropriate flow rate in order to make the process time efficient.

3.3. Effect of influent concentration of metal ions

The change in the influent metal ion concentration has a significant effect on breakthrough curve. The effect of influent concentration on the shape of the breakthrough curves and the column adsorption parameters was investigated. The value of pH was 5.0. Fig. 3 depicts the breakthrough curves of adsorption of copper(II) (a) and lead(II) (b) onto chaff at different

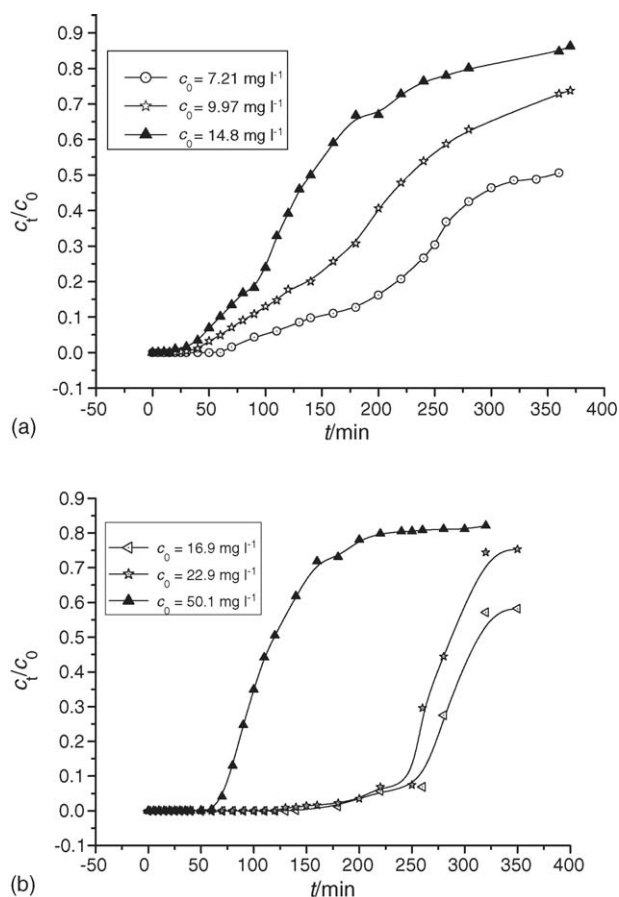


Fig. 3. The effect of influent concentration of copper(II) (a) and lead(II) (b) on biosorption by chaff ($v = 3.6 \text{ ml min}^{-1}$).

influent concentrations. In the interval of 300 min, the value of c_t/c_0 reached 0.45, 0.6 and 0.8 when influent concentration was 7.21 mg l^{-1} , 9.97 mg l^{-1} and 14.8 mg l^{-1} , respectively, for copper. At the same time, the value of c_t/c_0 reached 0.4, 0.55 and 0.8 when influent concentration was 16.9 mg l^{-1} , 22.9 mg l^{-1} and 50.1 mg l^{-1} , respectively, for lead.

As shown from the breakthrough curves in Fig. 3, adsorption capacity increase with influent metal ions concentration increasing and it would spend more time reaching the saturation. This can be explained by the fact that more adsorption sites were being covered as the metal ions concentration increasing. The larger the influent concentration the steeper is the slope of breakthrough curve and smaller is the breakthrough time. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time, or in other words, the diffusion process is concentration dependent. As the influent concentration increases, metal loading rate increases, so does the driving force for mass transfer, which in a decrease in the adsorption zone length [16].

3.4. Modeling of column study results: Thomas model

Thomas model was applied to the experimental data with respect to flow rate and influent concentration of metal ions. A

Table 1

Parameters predicted from Thomas model of copper biosorption at different influent concentration and different flow rate

c_0 (mg l^{-1})	v (ml min^{-1})	k_{Th} ($\text{ml min}^{-1} \text{ mg}^{-1}$)	q_0 (mg g^{-1})	R	S.D.
7.211	3.6	1.927×10^{-3}	1.89	0.995	0.101
9.974	3.6	1.560×10^{-3}	1.95	0.987	0.203
14.82	3.6	1.348×10^{-3}	1.98	0.971	0.303
14.82	5.6	2.271×10^{-3}	1.79	0.898	0.816
14.82	8.3	2.711×10^{-3}	1.67	0.950	0.313

Table 2

Parameters predicted from Thomas model of lead biosorption at different influent concentration and different flow rate

c_0 (mg l^{-1})	v (ml min^{-1})	k_{Th} ($\text{ml min}^{-1} \text{ mg}^{-1}$)	q_0 (mg g^{-1})	R	S.D.
16.93	3.6	1.882×10^{-3}	4.65	0.978	0.532
22.88	3.6	1.262×10^{-3}	5.88	0.979	0.457
50.12	3.6	4.144×10^{-4}	6.72	0.886	0.701
50.12	5.6	4.816×10^{-4}	5.98	0.826	0.798
50.12	7.5	5.507×10^{-4}	4.70	0.965	0.444

linear was plotted on each set of data to determine the coefficients from slope and intercept according to Eq. (2). Residual standard deviations (S.D.) of the linear Thomas form was also calculated. Inspection of each lines indicated that they were all fits with linear coefficients (R) ranging from 0.965 to 0.995 and lower S.D. (smaller than 1), except the line obtained from the flow rate was 3.6 ml min^{-1} , 5.6 ml min^{-1} of lead and the flow rate was 5.6 ml min^{-1} of copper for R . According to the linearized form of the Thomas model, the parameters of q_0 and k_{Th} were shown in Tables 1 and 2 for copper and lead cations, respectively.

From Tables 1 and 2, we can draw a conclusion that with the flow rate increasing, the value of k_{Th} became bigger, and the q_0 of equilibrium was rising. The influent mol-concentration of copper and lead were nearly equal ($c_{0-\text{Cu}} = 14.8 \text{ mg l}^{-1}$, $c_{0-\text{Pb}} = 50.1 \text{ mg l}^{-1}$ or $c_{0-\text{Cu}} = 0.233 \text{ mmol g l}^{-1}$, $c_{0-\text{Pb}} = 0.240 \text{ mmol l}^{-1}$), however, when reached equilibrium, the adsorptive capacity of copper and lead were equal approximately, only lead was a little big. This can be indicated that the mechanisms of copper and lead adsorbing by chaff are approximate for that they have the same charge. So in the process of biosorption ion-exchange probably occurs. With the increasing of influent concentration of copper and lead, the corresponding value of k_{Th} was decreasing and the column capacity q_0 of equilibrium was rising. So higher flow rate and lower influent concentration have disadvantage to adsorption of copper and lead on chaff column.

3.5. The competitive adsorption of copper(II) and lead(II)

In order to investigate the effect of coexistence ions on the adsorption of chaff, we did the following group of experiments, competitive adsorption of copper(II) and lead(II), which included three parts: after copper(II) saturation, lead(II) was adsorbed; after lead(II) saturation, then copper(II) was adsorbed; copper(II) and lead(II) were adsorbed simultaneously.

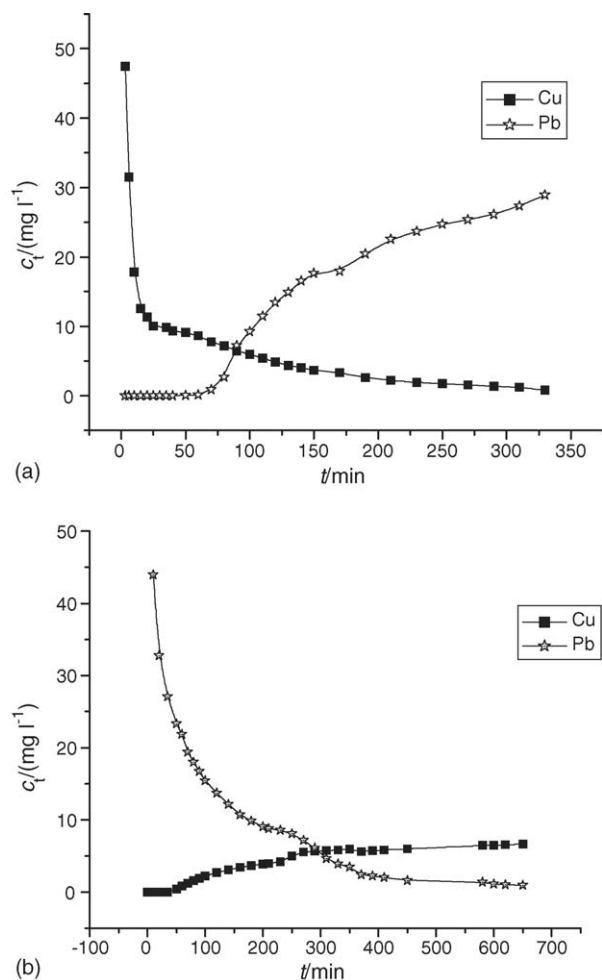


Fig. 4. After copper(II) saturation, then lead(II) adsorbed (a) and after lead(II) saturation, then copper(II) adsorbed (b) by chaff ($v = 5.6 \text{ ml min}^{-1}$).

3.5.1. The chaff column saturated by copper(II), then lead(II) solution passed through

In this experiment, we studied adsorption of copper(II) affected by lead(II). Firstly, the column of chaff was saturated by copper(II) solution of 9.97 mg l^{-1} , then lead(II) solution, equal mol-concentration with copper solution applied in this experiment (namely 32.5 mg l^{-1}), was passed through the column. The breakthrough curve was shown in Fig. 4a. It was plotted as the point of effluent concentration versus time. From Fig. 4a, it concluded that copper(II) be replaced by lead(II) from the column. This was because that the concentration of lead(II) was higher, lead(II) could competitive with copper(II) binding the adsorbing sites existed on the chaff. Furthermore, when lead(II) ions were adsorbed, a few copper(II) ions were desorbed in the same time.

3.5.2. The chaff column saturated by lead(II), then copper(II) solution passed through

In this part, we studied adsorption of lead(II) affected by copper(II). Firstly the column of chaff was saturated by lead(II) of 24.4 mg l^{-1} , then, the copper(II) solution, equal mol-concentration with lead solution applied in this experiment (namely 7.49 mg l^{-1}), was passed through the column. The

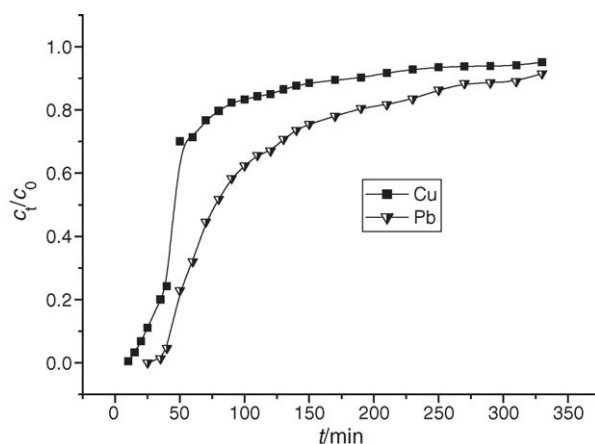


Fig. 5. Copper(II) and lead(II) adsorbed synchronously by chaff ($v = 3.6 \text{ ml min}^{-1}$).

breakthrough curve was shown in Fig. 4b. It also was plotted as the point of effluent concentration versus time. From Fig. 4b, it can be concluded that lead(II) was replaced by copper(II) from the chaff in the column. This was because that the concentration of copper(II) was higher, copper(II) can competitive with lead(II) binding the adsorbing sites existed on the chaff. Hence, when copper(II) ions were adsorbed, the corresponding lead(II) ions were desorbed.

From Fig. 4a and b, even the shape of them was very approximately, it also implied that the chaff preferred to adsorb lead cation than copper cation. For that in Fig. 4a the copper cation was desorbed quicker than that of lead cation in Fig. 4b, while adsorbed lead cation was much easier than copper cation.

3.5.3. Copper(II) and lead(II) adsorbed simultaneously

In this part, copper(II) and lead(II) adsorbed synchronously by chaff were studied. The content of solute was that the metal ions concentration of copper(II) and lead(II) were 14.7 mg l^{-1} and 50.6 mg l^{-1} , respectively. They were nearly equal mol-concentration, too. The breakthrough curves were shown in Fig. 5.

From the studies of the competitive adsorption of copper(II) and lead(II), we can come to a conclusion that the mechanism of the two metal ions is in homology nearly. The tendency for adsorbed lead(II) was higher than that for copper(II) by chaff at the initial process. While when reached near saturation, lead ions may need more time for that the value of k_{Th} of copper was higher than that of lead in the same conditions. By the time of 100 min, the change of C/C_0 according to copper was very slow, and as far as lead is concerned, it needs 200 min.

The Thomas model was used in this part experiment, the value of C/C_0 ranged from 0.01 to 0.83. The parameters of q_0 and k_{Th} in Thomas model were listed in Table 3.

Comparing Table 3 and Tables 1 and 2, we can observe that when dual-metals coexisted, the adsorption capacity and the value of k_{Th} per metal ion decreased comparing with single metal ion existence. Hence, in this condition the adsorptive rate decreased, too. While the results also indicated that the total adsorption capacity, namely, the sum of adsorption capacity

Table 3
The results of dual-metals competitive adsorption on chaff using Thomas model
($v = 3.6 \text{ ml min}^{-1}$)

Parameters	$c_0 \text{ (mg l}^{-1}\text{)}$	$k_{\text{Th}} \text{ (ml min}^{-1} \text{ mg}^{-1}\text{)}$	$q_0 \text{ (mg g}^{-1}\text{)}$	R	S.D.
Cu	14.74	1.316×10^{-3}	0.762	0.834	0.921
Pb	51.64	3.758×10^{-4}	3.81	0.974	0.260

both copper and lead did not obviously reduce. It was near to the value of single copper or lead existence. Furthermore the adsorption capacity of single copper and single lead ions was nearly equal (mmol g^{-1}). This suggested that whether single metal ions existence or dual-metals coexistence, all not affected the total adsorption capacity of biomass. So it proved that chaff can be used to remove many heavy metal ions coexisted in wastewater. This can enlarge the application range of chaff in practice.

3.6. Regeneration and elution of metals from loaded chaff biomass

Disposal of the exhausted adsorbent loaded with heavy metal ions creates another environmental problem as it is hazardous material which pollutes environment. This problem may be overcome to some extent by using one of the elimination (e.g. elution, incineration and pyrolysis) methods. The elution of heavy metals is the most common elimination method, allowing both recovery of solutions of heavy metal ions at higher concentrations for inertisation and recycling of the adsorbent for subsequent uses. The percent recoveries of the heavy metal ions by the elution method were calculated for single systems.

The use of chaff biomass as a potential biosorbent depends not only on the biosorptive capacity, but also on how well the biomass regenerated and used in the metals' recycling process, metal ions binding in the chaff should be desorbed at end of adsorption. Desorbed experiments were performed with 0.1 mol l^{-1} nitric acid solution as the desorbed agent. Fig. 6 was the desorbed curve.

As shown in Fig. 6a and b, copper(II) and lead(II) are both easily desorbed because in less than 100 min the desorption nearly completed. Furthermore, with the flow rate increasing, the desorbed process was quick. The nitric acid was effective in the elution of adsorbed metals.

3.7. Adsorption/desorption recycles onto chaff

Regeneration of the adsorbent material is of crucial importance in the economic development. The aim is to remove the loaded metal from the column in the smallest possible volume of an eluting solution. Regeneration must produce small volume of metal concentrates suitable for metal-recovery process, without damaging the capacity of the adsorbent, making it reusable in several adsorptions and desorption cycles. Fig. 7 shows the recycles of adsorbed metals by chaff. This study shows that chaff can be used repeatedly without significantly losing their adsorption capacity for metal ions of copper(II). But the capacity for lead(II) is decreased. The results indicate that following the suc-

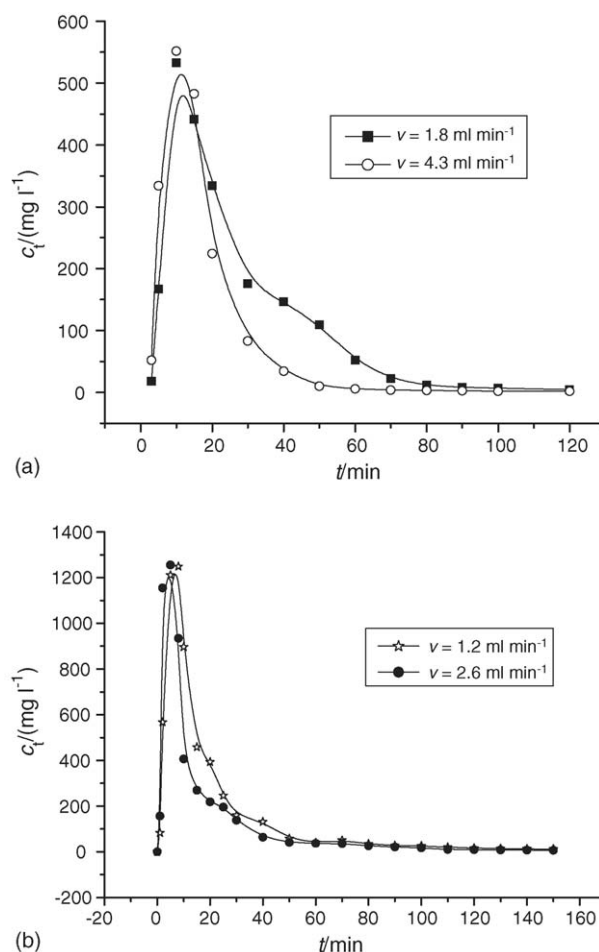


Fig. 6. Desorption of copper(II) (a) and lead(II) (b) at different flow on chaff.

cessful adsorption of heavy metals the chaff may be recovered for consecutive uses with advantage.

3.8. The Mechanism of biosorption by chaff

As we all known, the cell-wall of chaff has carboxyl, hydroxy and amidogen, etc., responsible for binding metal ions [11]. When biosorption occurs, ions-exchange occurs in the same time. Hydrogen ions in carboxyl, hydroxyl and amidogen were replaced by heavy metal ions. This is why we have found the value of pH has great effect on adsorption. As the adsorption reached equilibrium, the value of pH kept a constant range. Furthermore, $\text{mol-}q_0$ of copper and lead are nearly equal, maybe they have equal electric charge. But the value of k_{Th} was not equal either, so the biosorption mechanism of copper and lead was not in the same completely. Possibly this is because that they have different atomic weight, electronegativity, ionic semi-diameter, and they have different binding energy with the chaff. Pb(II) is classified as a class b ion, while Cu(II) are classified as borderline ions, so the behavior of adsorption is not full same [17]. In addition, adsorption/desorption recycles onto chaff indicate that acidification has advantage to the removal of copper, and ion-exchanged mechanism is important in metal binding on chaff. In the fact, the progress

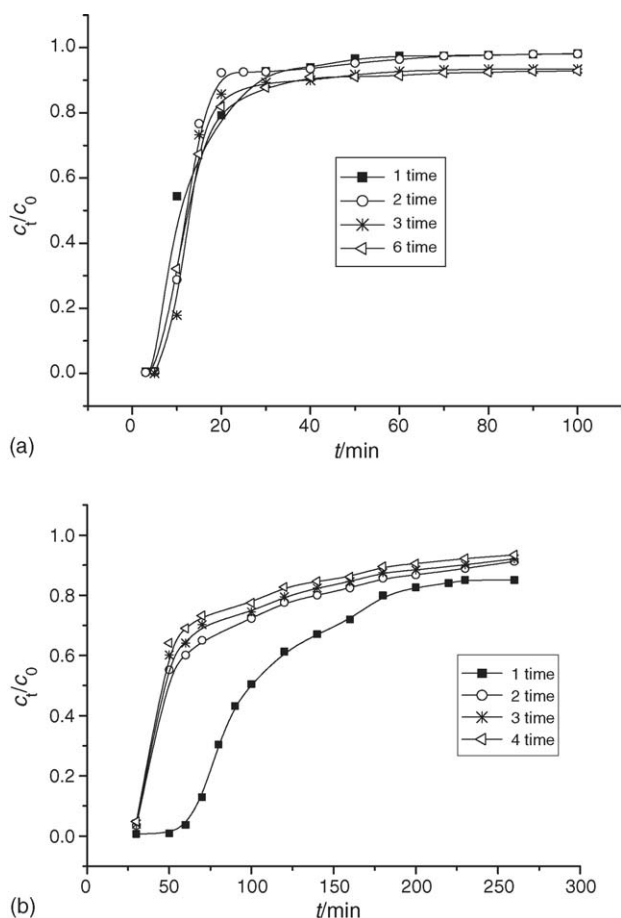


Fig. 7. Adsorption/desorption cycles onto chaff of copper(II) (a) and lead(II) (b) ($v = 3.6 \text{ ml min}^{-1}$, $c_{0-\text{Cu}} = 7.44 \text{ mg l}^{-1}$, $c_{0-\text{Pb}} = 50.1 \text{ mg l}^{-1}$).

of biosorption is very complex, furthermore study will be needed.

4. Conclusion

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

- The aim of this study is to use chaff as adsorbent to removal heavy metal ions from solution proved efficiently.
- The Thomas mathematical model adequately described the adsorption of copper(II) and lead(II) onto chaff by column mode.
- Copper(II) and lead(II) are both easily desorbed from chaff. Chaff can be recycled to remove heavy metal ions from solutions.
- For the adsorbent of chaff obtained from agriculture as a by-product, the treatment method is expected to be economical and environmental.

Acknowledgement

The authors express their sincere gratitude to the Henan Science and Technology Department in China, for the financial support of this study.

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