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Separation of Pb^{2+} from Mg^{2+} by modified sugarcane bagasse under batch and column conditions: Effect of initial concentration ratio

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Abstract Effect of initial concentration ratio ($C_0^{\text{Mg}} : C_0^{\text{Pb}}$) on separation of Pb^{2+} from Mg^{2+} by the modified sugarcane bagasse was carried out under batch and column conditions. For comparison, the adsorption performance of the modified SCB (sugarcane bagasse) for Pb^{2+} in one component system was studied under the two conditions. Amount of Pb^{2+} and Mg^{2+} adsorbed on the column in the binary system was calculated through the elution curves. Results showed that the adsorption capacity of Pb^{2+} (q_e^{Pb}) decreased while that of Mg^{2+} (q_e^{Mg}) increases with the increase of $C_0^{\text{Mg}} : C_0^{\text{Pb}}$, and good linear relationships between $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ and $q_e^{\text{Mg}}/q_e^{\text{Pb}}$ were obtained under both conditions. According to the linear equations, mass ratio of metal ions adsorbed on the modified SCB was calculated. It was observed that mass ratio was higher than 95% for Pb^{2+} at $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 0.022$ while for Mg^{2+} at $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$ under batch condition. Under the column condition, high mass ratio (>95%) for Pb^{2+} and Mg^{2+} was obtained at $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 1.24$ and $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 585.5$, respectively. The above results showed that modified SCB could be used to separate Pb^{2+} and Mg^{2+} when $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 1.24$ (Pb^{2+} adsorbed selectively) or $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$ (Mg^{2+} adsorbed selectively). These findings would provide theoretical guidance for separation of metal ions.

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1. Introduction

With the development the society, large amounts of wastewater containing heavy metals were discharged from printing, electroplating, leather tanning, mining and pigments industries (Ghaedi et al., 2006; Anayurt et al., 2009). Among these heavy metal ions, lead in particular is the most important pollutants, which would cause severe damage to the human kidney, nervous system, reproductive system, liver, and brain even at low concentration (Xu et al., 2008). Moreover, it is non-biodegradable and tends to accumulate in organisms as part of

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the food chain (Motsa et al., 2011; Deng et al., 2013). Efforts for effective lead removal from wastewater have been continuously made for decades. A variety of methods, including chemical precipitation, membrane process, coagulation, phyto-extraction, and adsorption had been reported to remove lead from aqueous solution (Isaac et al., 1997). Among these methods, adsorption is recognized as an efficient and economic method.

Recently, more and more attention was paid on biosorbents, especially on the agricultural waste such as sugarcane bagasse, leaf and orange peel due to its low cost and ready availability (Yuvaraja et al., 2014; Madala et al., 2015; Lasheen et al., 2012; Hossain et al., 2012; Wan Ngah and Hanafiah, 2008). However, the application of untreated agricultural waste has drawbacks such as low adsorption capacity and poor adsorption selectivity (Nguyen et al., 2013). In order to improve its adsorption capacity for metal ions, different kinds of modified biosorbent were prepared. Yu et al. (2015a) had reported that the adsorption capacity of sugarcane bagasse for Pb^{2+} increased from 0.04 to 1.06 mmol g^{-1} after modification by pyromellitic dianhydride. Zheng et al. (2011) had reported that the maximum sorption capacity of cotton for Pb(II) increased to 2.45 mmol g^{-1} after grafted by polyacrylic acid sodium. Feng et al. (2011) found that the grafted copolymerization of orange peel increased the metal uptake of Pb(II) up to 4.2 times. The adsorption capacity of the sorbents for Pb^{2+} increased significantly after modification by functional groups. Even so, the application of biosorbent still encounters many problems, especially the selective adsorption from the co-ions. In real industrial wastewater, it contains not only heavy metals but also high concentration of other metal ions, such as Mg^{2+} , Ca^{2+} , K^+ and Na^+ . Contreras et al. (2006) had reported that Pb^{2+} binding decreased as the comparative concentration ratio of Mg^{2+} increased to a certain value. Sawalha et al. (2009) found that the binding of Pb^{2+} would be hindered by combined concentrations of Ca and Mg higher than 40.0 mmol L^{-1} . Reddy et al. (2010) explored that as the initial concentration ratio of the alkali metal ions increased, the uptake of Pb(II) ions by modified *Moringa oleifera* leaves decreased. Results above showed that concentration ratio of co-ions had great effect on the adsorption of Pb^{2+} in the binary system. However, the effects of concentration ratio on the adsorption of co-ions still needed to be investigated in details, and the optimum conditions for Pb^{2+} and common co-ions separation by the modified sorbent under batch and column conditions should be determined.

In previous study, pyromellitic dianhydride modified SCB with high adsorption capacity for heavy metal ions had been prepared (Yu et al., 2015b). In this study, Mg^{2+} was chosen as the model co-ions for its a common interfering ion, and effects of $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ on Pb^{2+} and Mg^{2+} adsorption in the Mg/Pb binary system were carried out on the modified SCB under the batch and column conditions. For comparison, the adsorption kinetic and isotherm of Pb^{2+} in one component system were studied under the two conditions. Breakthrough curves of Pb^{2+} at different $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ in the binary system were depicted. The amount of Pb^{2+} and Mg^{2+} adsorbed on the modified SCB fixed bed column was calculated through the elution curves by using ethylenediaminetetraacetic acid disodium salt as the eluent. The relationship between $C_0^{\text{Mg}}/C_0^{\text{Pb}}$ and the adsorption capacity ratio of the two metal ions ($q_e^{\text{Mg}}/q_e^{\text{Pb}}$) was discussed. The optimum condition for Pb^{2+} and Mg^{2+} separation under the batch and column conditions was concluded.

2. Materials and methods

2.1. Materials

Sugarcane bagasse was dried and ground to pass through a 100-mesh sieve, and then it was washed with ethanol and distilled water, and dried at 60 °C for 24 h before use. Pyromellitic dianhydride (PMDA) and ethylenediaminetetraacetic acid

disodium salt were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Solutions of lead and magnesium were prepared using the corresponding metal nitrate.

2.2. Surface modification

The modified SCB was prepared according to Yu et al. (2015a). A 1.0 g of PMDA and 1.0 g of SCB were added into a round-bottomed flask containing 30 mL of N,N-dimethylacetamide. After stirring at 50 °C for 4 h, the modified SCB was obtained, and it was washed in order with NaOH (0.01 mol L^{-1}) and water. Then it was dried and stored in a desiccator before use.

2.3. Batch adsorption experiment

Adsorption performances including isotherm and kinetic experiment were carried out at 28 °C and 150 rpm on an orbital shaker. In the isotherm experiment, 0.005 g of the modified or unmodified SCB was added into a 20 mL of Pb^{2+} solution with initial concentration ranged from 0.05 to 1.21 mmol L^{-1} at pH ranged from 5.0 to 5.15 adjusting by using HCl and NaOH solution. In the kinetic experiment, 0.010 g of the modified SCB was added into 80 mL of Pb^{2+} solution with the initial concentration of 1.00 mmol L^{-1} (pH = 5.0). Effect of Mg^{2+} on the adsorption of Pb^{2+} was carried out in the binary system. In this system, initial concentration of Pb^{2+} was fixed at 0.12 mmol L^{-1} , and concentration of Mg^{2+} ranged from 0.001 to 37.6 mmol L^{-1} . The residual concentration of metal ions after adsorption was determined by atomic absorption spectrophotometer (AA6300, Shimadzu, Japan). The adsorption isotherms of Pb^{2+} and Mg^{2+} were fitted by Langmuir model (Eq. (1))

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the amount of dyes adsorbed per gram of sorbent at equilibrium (mmol g^{-1}), q_m is the maximum amount of adsorption (mmol g^{-1}), K_L is the Langmuir biosorption constant (L mmol^{-1}), and C_e is the equilibrium concentration of substrates in the solution (mmol L^{-1}).

2.4. Fixed bed column adsorption experiment

The fixed bed column adsorption experiment was conducted at room temperature in a glass column with an internal diameter of 1 cm and length of 20 cm. 1.0 g of the modified SCB was accurately weighed and soaked in 100 mL of distilled water for 30 min before being poured slowly into the column. After the adsorbent had settled, the column was pumped with distilled water for 30 min (bed height: 12.1 cm). In the dynamic adsorption experiment, the solution of metal ions was pumped using a peristaltic pump (YZ1515X, Longer pump), connected with Teflon tubes from the sample tank to the bottom of the column at the designated flow rate (up flow pattern). Flow rate of the sample in the experiment was fixed at 6.25 mL min^{-1} . Solution pH was in the range of 5.0–5.15. The concentration of Pb^{2+} used in the experiment was all fixed at 0.12 mmol L^{-1} . In the binary system, mixture solutions of Mg^{2+} and Pb^{2+} with mass concentration ratios of 1:1, 10:1, 20:1, 50:1 and 100:1 were pumped into the fixed bed column. Samples were

collected at the exit of the column at different time intervals and analyzed for metal ion concentrations by using atomic absorption spectrophotometer. The amount of metal ions adsorbed on the fixed bed column at time t (q_t , mmol g^{-1}) could be calculated by the following equation (integrated by using the software origin 8.0):

$$q_t = \frac{v \int_{t=0}^{t=t} (C_0 - C_t) dt}{m} \quad (2)$$

where v (mL min^{-1}) is the volumetric flow rate. C_t (mmol L^{-1}) is the concentration of metal ion in the effluent at time t . C_0 (mmol L^{-1}) is the inlet concentration of metal ion, and m is the mass of the modified SCB used in the fixed bed column.

2.5. Fixed bed column desorption experiment

After exhaustion of the modified SCB fixed bed column, desorption experiment was carried out by pumping ethylenediaminetetraacetic acid disodium salt (EDTA-2Na, 0.02 mol L^{-1}) as eluent at flow rate of 6.25 mL min^{-1} . Concentrations of Mg^{2+} and Pb^{2+} in the eluate at time t (C'_t , mmol L^{-1}) were determined. The amount of metal ions desorbed at time t (q'_t , mmol g^{-1}) could be calculated by Eq. (3).

$$q'_t = \frac{v \int_{t=0}^{t=t} C'_t dt}{m} \quad (3)$$

3. Results and discussion

3.1. Batch adsorption experiment in one component system

Adsorption isotherms of Pb^{2+} showed that the adsorption capacity was increased obviously after modification. According to Langmuir model, the maximum amount of metal ions adsorbed on the unmodified and modified SCB was $0.18\text{--}0.74 \text{ mmol g}^{-1}$, respectively (data was not shown). The increased adsorption capacity was due to the introduction of the large amount of carboxyl groups, which provide the active sites for Pb^{2+} adsorption (Yu et al., 2013). Adsorption kinetic of Pb^{2+} on the modified SCB showed that the adsorption is a rapid process, and it could complete within 60 min (data was not shown). According to the pseudo-second order model, the adsorption rate was $1.04 \text{ g mmol}^{-1} \text{ min}^{-1}$.

3.2. Effects of the initial concentration ratio on Pb^{2+} and Mg^{2+} separation under the batch condition

In this experiment, the initial concentration of Pb^{2+} was fixed at 0.12 mmol L^{-1} , and concentration of Mg^{2+} ranged from 0.001 to 37.6 mmol L^{-1} . Inset in Fig. 1 shows the amount of Mg^{2+} and Pb^{2+} adsorbed on the modified SCB in the binary system. The adsorption amount of Mg^{2+} increased with the increase of $C_0^{\text{Mg}} : C_0^{\text{Pb}}$, while that of Pb^{2+} decreased with it. The increased Mg^{2+} adsorption was due to its high initial concentration providing an important driving force to overcome the mass transfer resistance between the aqueous and solid phase (Aksu and Tezer, 2000). The decrease in Pb^{2+} adsorption was due to competitive inhibition effect. The inhibition of Mg^{2+} on the adsorption of Pb^{2+} had been reported by Spinti et al. (1995) and Chandra et al. (2003).

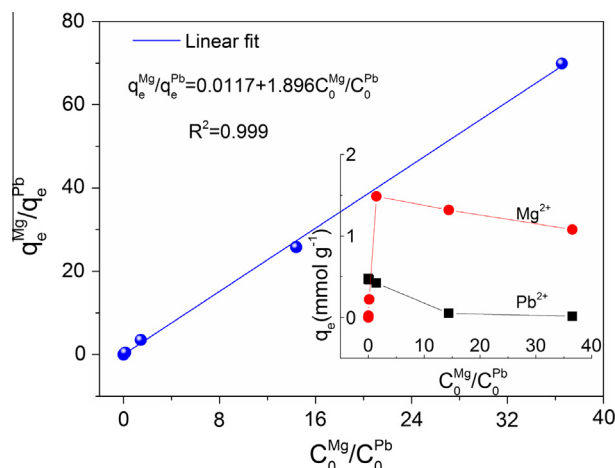


Figure 1 Linear relationship between initial mass concentration ratio and adsorption capacity ratio of the two metal ions under batch condition. Inset: amount of Mg^{2+} and Pb^{2+} adsorbed on the modified SCB at different initial concentration ratios of the two metal ions.

It was interesting to find that $q_e^{\text{Mg}} : q_e^{\text{Pb}}$ increased linearly with the increase of $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ (shown in Fig. 1). Similar results had been observed in the previous study (Yu et al., 2015c, 2012). Since the adsorption capacity of the two metal ions was decided by their initial concentration ratio, the mass ratio of Pb^{2+} and Mg^{2+} adsorbed on the modified SCB was calculated from the values of $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ (Eqs. (4) and (5)) and shown in Fig. 6.

$$\text{Mass ratio of } \text{Pb}^{2+} = \frac{1}{1.0117 + 1.896 C_0^{\text{Mg}}/C_0^{\text{Pb}}} \quad (4)$$

$$\text{Mass ratio of } \text{Mg}^{2+} = \frac{0.0117 + 1.896 C_0^{\text{Mg}}/C_0^{\text{Pb}}}{1.0117 + 1.896 C_0^{\text{Mg}}/C_0^{\text{Pb}}} \quad (5)$$

At $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 0.022$, the mass ratio of Pb^{2+} was higher than 95%, while at $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$, the mass ratio of Mg^{2+} was higher than 95%. That means Pb^{2+} could be adsorbed selectively from the mixture solution at $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 0.022$, while Mg^{2+} could be adsorbed selectively at $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$. The two metal ions could be separated by the modified SCB when $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 0.022$ or $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$. At $0.022 < C_0^{\text{Mg}} : C_0^{\text{Pb}} < 10.01$, the two metal ions interfered each other seriously, and Mg^{2+} and Pb^{2+} could not be separated directly by modified SCB under the batch condition.

3.3. Adsorption of Pb^{2+} on the modified SCB fixed bed column in one component system

Fig. 2 shows the breakthrough curve of Pb^{2+} on the modified SCB fixed bed column. It was observed that the breakthrough curve showed an obvious “S” shape. Pb^{2+} was removed completely from the aqueous solution at the beginning due to the large amount of unoccupied active sites (carboxyl groups), and C_t/C_0 was much lower than 0.05 in this period. With the occupation of carboxyl groups, large amount of Pb^{2+} could not be adsorbed and begin to flow out of the column, and

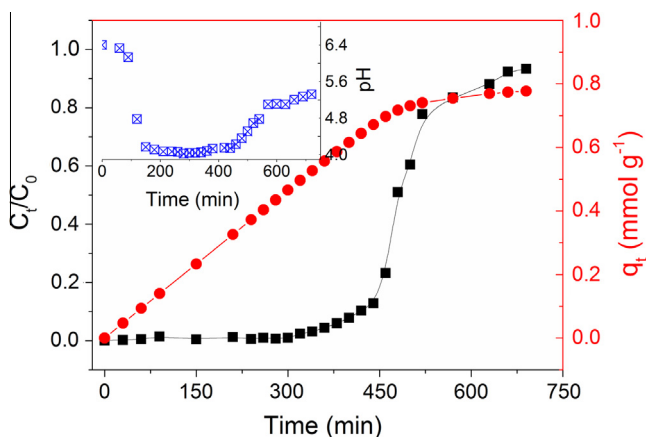


Figure 2 Breakthrough and adsorption kinetic curves of Pb^{2+} on the modified SCB fixed bed column. Inset: variation of pH during the dynamic adsorption process (amount of sorbent = 0.5 g, inlet concentration of Pb^{2+} = 0.12 mmol L^{-1} , flow rate = 6.25 mL min^{-1}).

C_t/C_0 increased sharply to 1.0 till the column exhausted. The amount of Pb^{2+} adsorbed at time t (q_t) was calculated according to Eq. (1) and shown in Fig. 2. It was observed that the saturated capacity of the column was 0.78 mmol g^{-1} , which was close to that obtained in the batch experiment.

Inset in Fig. 2 shows the variation of pH during this dynamic adsorption process. It was observed that pH dropped firstly to a platform at about 4.0 and then increased slowly to the initial pH. As the initial rate of adsorption was faster, the amount of binding metals onto the sorbent was larger. Hydrogen ions were released into solution through the reaction (R1), and the values of pH decreased rapidly at the initial process. Similar reports had been reported by Vilar et al. (2008) and Han et al. (2006).



By using Eq. (6), the amount of H^+ released was calculated to be 0.956 mmol g^{-1} , which demonstrated that 0.478 mmol g^{-1} of active site was provided by $-\text{COOH}$ and the other amount of 0.302 mmol g^{-1} (total amount: 0.78 mmol g^{-1}) was provided by $-\text{COO}^-$ and the other functional groups.

$$q_t^{\text{H}^+} = \frac{v \int_{t=0}^{t=t} (C_0^{\text{H}^+} - C_t^{\text{H}^+}) dt}{m} \quad (6)$$

3.4. Effects of the initial concentration ratio on Pb^{2+} adsorption on the modified SCB fixed bed column

The effect of the initial mass concentration ratio on the adsorption of Pb^{2+} in the binary system was conducted on the fixed bed column. Fig. 3a shows that breakthrough curves were dispersed and breakthrough occurred more slowly at low $C_0^{\text{Mg}} : C_0^{\text{Pb}}$, while sharply breakthrough curves were obtained at high $C_0^{\text{Mg}} : C_0^{\text{Pb}}$. The breakthrough time ($C_t/C_0 = 0.05$) of Pb^{2+} decreased obviously from 300 min to 210 and 5 min when $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ increased from 1:1 to 10:1 and 100:1, and the amount of Pb^{2+} adsorbed decreased from 0.66 to 0.50 and 0.13 mmol g^{-1} (shown in Fig. 3b).

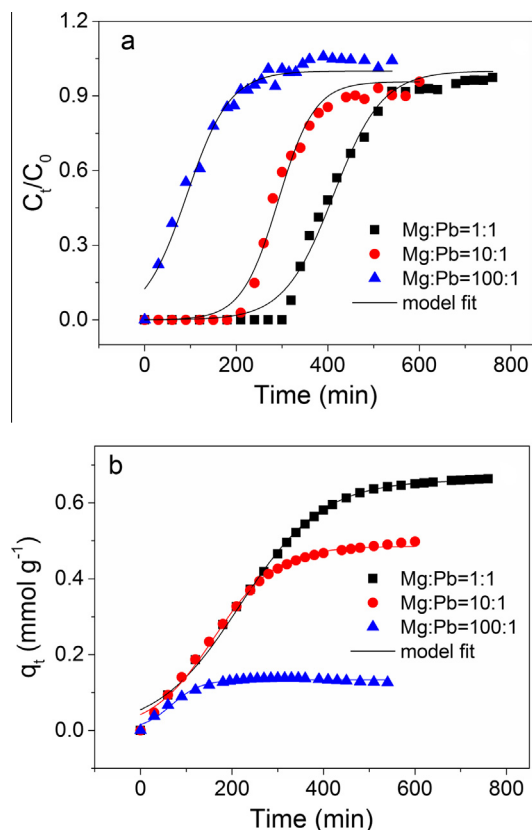


Figure 3 Effects of the concentration ratios on the (a) breakthrough curve and (b) adsorption kinetic of Pb^{2+} on the modified SCB fixed bed column (amount of sorbent = 0.5 g, inlet concentration of Pb^{2+} = 0.12 mmol L^{-1} , $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 1 : 1, 10:1$ and 100:1, flow rate = 6.25 mL min^{-1}).

In order to describe the fixed-bed column behavior and scale it up for industrial applications, the breakthrough curves of Pb^{2+} were fitted by Bohart-Adams model (Eqs. (7)–(9)) (Baral et al., 2009; Aksu and Gonon, 2004; McKay and Bino, 1990).

$$\frac{C_t}{C_0} = \frac{e^{k_{AB}C_0t}}{e^{k_{AB}N_0Z/U} - 1 + e^{k_{AB}C_0t}} = \frac{1}{1 + (e^{k_{AB}N_0Z/U} - 1) \times e^{-k_{AB}C_0t}} = \frac{1}{1 + b \exp(-kt)} \quad (7)$$

$$b = e^{k_{AB}N_0Z/U} - 1 \quad (8)$$

$$k = k_{AB}C_0 \quad (9)$$

where k_{AB} (L mg^{-1} min^{-1}) is the kinetic constant, N_0 (mg L^{-1}) is the maximum volumetric sorption capacity, U (cm min^{-1}) is the linear flow rate, and Z (cm) is the bed depth in the column. Calculated constants are listed in Table 1. It was observed that the model fitted the curves well. k_{AB} obtained in the single ion system was higher than that obtained in the binary system, demonstrating that the presence of Mg^{2+} inhibits the adsorption of Pb^{2+} . Since all the breakthrough curves matched the Bohart-Adams model well, the attempt to find the relationship between q_t and time t was tried by using a modified Bohart-Adams model (Eq. (10)).

Table 1 Calculated parameters by using Bohart-Adams and modified Bohart-Adams models for the dynamic adsorption of Pb^{2+} on the modified SCB fixed bed column.

Constants	Concentration ratio ($C_0^{\text{Mg}} : C_0^{\text{Pb}}$)			
	Single ion	1:1	10:1	100:1
<i>Breakthrough curves (Bohart-Adams model)</i>				
R^2	0.983	0.988	0.977	0.975
b	$3.3 \times 10^6 \pm 4.4 \times 10^6$	2159.6 ± 1134.3	689.75 ± 445	6.99 ± 1.25
k (min^{-1})	0.03 ± 0.003	0.019 ± 0.001	0.022 ± 0.002	0.022 ± 0.002
<i>q_t curves (modified Bohart-Adams model)</i>				
R^2	0.994	0.995	0.994	0.977
q_m (mmol g^{-1})	0.79 ± 0.01	0.66 ± 0.004	0.49 ± 0.004	0.13 ± 0.001
b'	12.18 ± 1.17	11.08 ± 0.97	10.51 ± 1.03	7.68 ± 1.5
k' (min^{-1})	0.01 ± 0.0004	0.11 ± 0.0004	0.015 ± 0.0006	0.03 ± 0.003

$$q_t = \frac{q_m}{1 + b' \exp(-k't)} \quad (10)$$

where b' and k' (min^{-1}) are the adsorption constants, and q_m is the calculated adsorption capacity of the sorbent in the dynamic system. The estimated constants are listed in Table 1. High values of R^2 were obtained in all the systems. The calculated q_m at $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 1 : 1, 10:1$ and $100:1$ were 0.66, 0.49 and 0.13 mmol g^{-1} , which were very close to the experimental results: 0.66, 0.50 and 0.13 mmol g^{-1} , demonstrating that the adsorption kinetic curves could be predicted well by the modified Bohart-Adams model.

3.5. Desorption of Pb^{2+} and Mg^{2+} from the saturated fixed bed column

In order to further verify the adsorption capacity of Pb^{2+} and determine the amount of Mg^{2+} adsorbed on the column, desorption of the saturated columns was conducted by using EDTA-2Na (0.02 mol L^{-1}) as the eluent. Desorption of metal ions by EDTA-2Na was due to its strong coordination ability with Pb^{2+} and Mg^{2+} ($\lg K_{\text{Pb-EDTA}} = 18.04, \lg K_{\text{Mg-EDTA}} = 8.7$). The adsorbed metal ions (through electrostatic attraction with the carboxyl groups) on the sorbent surface would coordinate with EDTA-2Na and be released from the sorbent surface into the eluent. Fig. 4a and b depicts the desorption curves of the two metal ions from the saturated column obtained at different $C_0^{\text{Mg}} : C_0^{\text{Pb}}$. The completion of Pb^{2+} desorption was after 10 min, while that for Mg^{2+} was after 40 min. The fast desorption rate of Pb^{2+} may be due to its higher coordinating ability to EDTA. The desorption amount of the two metal ions (q_t') at different $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ was calculated according to Eq. (2) and shown in inset of Fig. 4a and b. The obtained desorption amounts of Pb^{2+} were very close to those obtained in the adsorption process, demonstrating the high desorption efficiency of EDTA-2Na. It was observed that when $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ varied from 1:1 to 10:1 and 100:1, q_t' of Pb^{2+} decreased from 0.60 to 0.49 and 0.12 mmol g^{-1} , while that of Mg^{2+} increased from 0.058, 0.26 and 0.41 mmol g^{-1} , respectively. The key role of the initial concentration on the adsorption of the two metal ions was further confirmed.

Since $q_e^{\text{Mg}} : q_e^{\text{Pb}}$ increased linearly with the increase of $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ in the batch system, the relationship was also tested in the column system. Fig. 5 depicts the effects of $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ on

the values of $q_e^{\text{Mg}} : q_e^{\text{Pb}}$. High values of R^2 demonstrated the equation fitted the data well. In order to further examine the model accuracy, comparison of theoretical predictions with experimental values of Pb^{2+} and Mg^{2+} sorption on the fixed bed column was carried out. Fig. 4c and d shows desorption curves and kinetics of the two metal ions from the saturated column obtained at $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 20 : 1$ and $50:1$. It was observed that the desorption amount of Pb^{2+} and Mg^{2+} at $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 20 : 1$ was 0.21 and 0.22 mmol g^{-1} , while that at $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 50 : 1$ was 0.14 and 0.25 mmol g^{-1} , respectively. The predicted and experimental values $q_e^{\text{Mg}} : q_e^{\text{Pb}}$ are shown in Fig. 5. Results showed that $q_e^{\text{Mg}} : q_e^{\text{Pb}}$ calculated were in excellent consistent with those obtained experimentally, demonstrating the feasibility of the linear equation under column condition. According to the linear equation, mass ratio of Pb^{2+} and Mg^{2+} was calculated by Eqs. (11) and (12) and is shown in Fig. 6. The mass ratio of Pb^{2+} adsorbed was higher than 95% when $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 1.24$, while that of Mg^{2+} was higher than 95% when $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 585.5$. Pb^{2+} and Mg^{2+} could be adsorbed selectively from the mixture solution at $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 1.24$ and $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 585.5$, respectively. The two metal ions could not be separated by the column when $1.24 < C_0^{\text{Mg}} : C_0^{\text{Pb}} < 585.5$.

$$\text{Mass ratio of } \text{Pb}^{2+} = \frac{1}{1.011 + 0.034 C_0^{\text{Mg}} / C_0^{\text{Pb}}} \quad (11)$$

$$\text{Mass ratio of } \text{Mg}^{2+} = \frac{0.011 + 0.034 C_0^{\text{Mg}} / C_0^{\text{Pb}}}{1.011 + 0.034 C_0^{\text{Mg}} / C_0^{\text{Pb}}} \quad (12)$$

Fig. 7 compares the mass ratio of metal ions adsorbed on the modified SCB under the batch and column conditions, respectively. It was observed that different $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ range for Pb^{2+} and Mg^{2+} separation (mass ratio > 95%) was obtained, which may be due to the different experimental condition. In batch experiment, concentration of the metal ions decreased gradually with the completion of the adsorption, while inlet concentration was kept at a constant value in the whole process under the column experiment. However, the reason why different separation and enrichment effects obtained under the two conditions still needed to be investigated comprehensively. Either in batch or in column conditions, initial concentration ratios played a key role in the adsorption of the two metal ions.

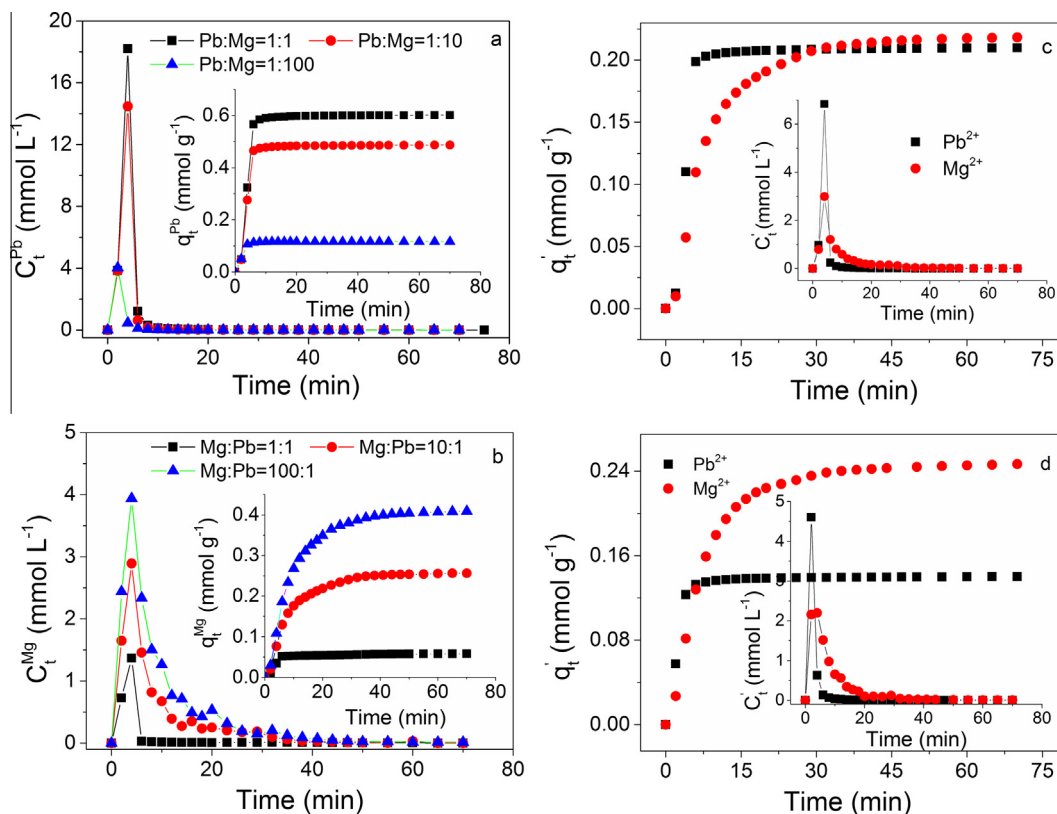


Figure 4 Desorption curves of (a) Pb^{2+} and (b) Mg^{2+} from the saturated column obtained at $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 1 : 1, 1:10$ and $1:100$ (inset: desorption kinetic curves of Pb^{2+} and Mg^{2+}), and desorption kinetic curves of Pb^{2+} and Mg^{2+} at (c) $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 20 : 1$ and (d) $C_0^{\text{Mg}} : C_0^{\text{Pb}} = 50 : 1$ (inset: desorption curves of Pb^{2+} and Mg^{2+}).

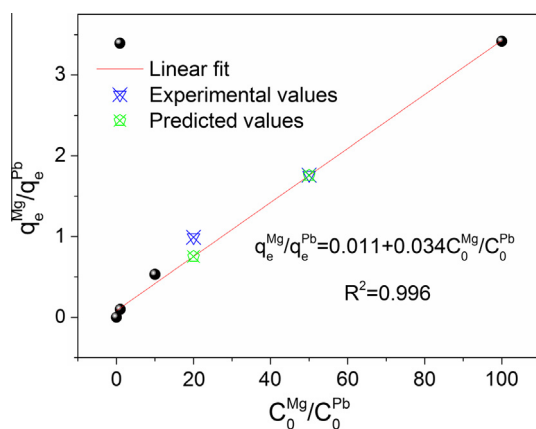


Figure 5 Linear relationship between initial mass concentration ratio and adsorption capacity ratio of the two metal ions under column condition.

Pb^{2+} could be easily adsorbed selectively from the mixture solution at low $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ under the column condition due to the fact that the metal has the larger atomic weight (207.2) and the more electronegative (Pb: 2.33 and Mg: 1.31) and the smaller hydrated ionic radii (Pb: 0.401 nm and Mg: 0.428 nm). Mg^{2+} could be easily separated at high $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ values under batch condition due to the strong salt-effect. By considering the results obtained in the batch and dynamic

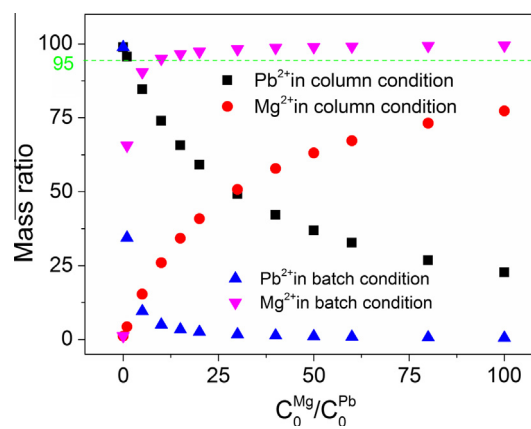


Figure 6 Mass ratio of metal ions adsorbed on the modified SCB under the batch and column conditions.

conditions, it was preferred to separate Pb^{2+} and Mg^{2+} under column condition when $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 1.24$ (Pb^{2+} adsorbed selectively), and separate the two metal ions under batch condition when $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$ (Mg^{2+} adsorbed selectively). Pb^{2+} and Mg^{2+} could not be separated directly by the modified SCB in both conditions when $1.24 < C_0^{\text{Mg}} : C_0^{\text{Pb}} < 10.01$. These findings illustrated that separation experimental condition was decided by the initial concentration ratio of the two metal ions.

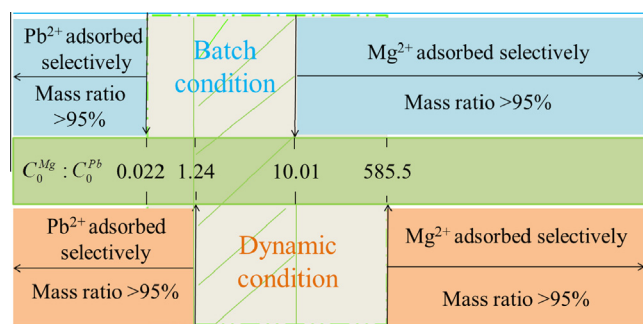


Figure 7 Comparison of mass ratio of Pb^{2+} and Mg^{2+} (>95%) obtained under batch and column condition.

4. Conclusions

Batch adsorption experiment showed that adsorption of Pb^{2+} decreased while Mg^{2+} increased with the increase of $C_0^{\text{Mg}}/C_0^{\text{Pb}}$. A good linear relationship between $C_0^{\text{Mg}}/C_0^{\text{Pb}}$ and $q_e^{\text{Mg}}/q_e^{\text{Pb}}$ was obtained. The slope and intercept of the fitted linear equation were 1.896 and 0.0117, respectively. Column experiments also illustrated that the initial concentration ratios played a key role in adsorption of the two metal ions. Breakthrough curves of Pb^{2+} at different $C_0^{\text{Mg}} : C_0^{\text{Pb}}$ in the binary system fitted Bohart-Adams model well and the adsorption kinetic curves of Pb^{2+} fitted the modified Bohart-Adams model well. The amount of Pb^{2+} and Mg^{2+} adsorbed on the modified SCB fixed bed column in the binary system was calculated through the elution curves. Also good linear relationship between $C_0^{\text{Mg}}/C_0^{\text{Pb}}$ and $q_e^{\text{Mg}}/q_e^{\text{Pb}}$ was obtained under the column condition. However, the slope and intercept of the fitted equation varied to 0.011 and 0.034, respectively. The different linear equations obtained under the different conditions illustrated that different mass ratio of Pb^{2+} and Mg^{2+} would be obtained at the same $C_0^{\text{Mg}}/C_0^{\text{Pb}}$. According to the values of mass ratio, it was concluded that Pb^{2+} and Mg^{2+} could be separated by the modified SCB at $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 0.022$ or $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$ under batch condition, and the range changed to $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 1.24$ or $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 585.5$ under the column condition. Separation of Pb^{2+} and Mg^{2+} would be preferred to conduct at column condition when $C_0^{\text{Mg}} : C_0^{\text{Pb}} < 1.24$ (Pb^{2+} adsorbed selectively), while conducted at batch condition when $C_0^{\text{Mg}} : C_0^{\text{Pb}} > 10.01$ (Mg^{2+} adsorbed selectively).

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