

Effects of co-ion initial concentration ratio on removal of Pb^{2+} from aqueous solution by modified sugarcane bagasse

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Abstract—A modified sugarcane bagasse (SCB) fixed bed column was used to remove Pb^{2+} from aqueous solution. To determine the optimal condition for Pb^{2+} separation, Ca^{2+} was chosen as the model interfering ion, and effects of Ca^{2+} and Pb^{2+} initial concentration ratio ($C_0^{\text{Ca}} : C_0^{\text{Pb}}$) on the adsorption of Pb^{2+} were investigated. Results showed that adsorption amount ratio of Ca^{2+} and Pb^{2+} ($q_e^{\text{Ca}} : q_e^{\text{Pb}}$) had a good linear relationship with $C_0^{\text{Ca}} : C_0^{\text{Pb}}$. Mass ratio of Pb^{2+} absorbed on the modified SCB was higher than 95% at $C_0^{\text{Ca}} : C_0^{\text{Pb}} < 1.95$, illustrating that Pb^{2+} could be selectively removed from aqueous solution. To verify that, simulated waste water containing co-ions of K^+ , Na^+ , Cd^{2+} and Ca^{2+} was treated, and results showed that the equilibrium amount of Pb^{2+} , K^+ , Na^+ , Cd^{2+} and Ca^{2+} adsorbed was 134.14, 0.083, 0.058, 1.28, and 1.28 mg g^{-1} , respectively, demonstrating that the modified SCB could be used to remove Pb^{2+} from aqueous solution in the investigated range.

Keywords: Sugarcane Bagasse, Fixed Bed Column, Adsorption, Pb^{2+} , Ca^{2+}

INTRODUCTION

Heavy metals pollution is of growing concern because of potential damaging effect on public health [1-3]. Among the heavy metals, lead is the most significant toxin and it tends to accumulate in food chain and ecosystems, which leads to irreversible brain damage [4-6]. Lead does not take part in biological processes and it is not biodegradable, which would accumulate in living tissues when the tolerance levels are exceeded [7,8]. Methods principally including chemical precipitation, membrane filtration, coagulation, adsorption and biosorption have been used to remove heavy metals from aqueous solution [8-10]. Among these, biosorption has many prominent advantages, including low initial cost, minimization of chemical pollution, and abundant sources [11-13]. Recently, agricultural byproducts such as sugarcane bagasse (SCB) have been used widely as biosorbent to remove heavy metals, especially Pb^{2+} , from aqueous solution [14-16]. However, biosorption of Pb^{2+} is influenced by various factors, including pH, biosorbent dosage, experimental temperature, initial concentration, contact time [9,17-19], especially the co-ions. The composition in Pb^{2+} polluted wastewater is extremely complicated in that various kinds of co-ions, including other heavy metal ions, alkaline-earth metal ions, and alkali metal ions, co-exist. Among them, Na^+ , K^+ , Mg^{2+} and Ca^{2+} are the most common co-ions with high concentration, and they have negative effect on the adsorption of Pb^{2+} . Nabizadeh [20] reported that the inhibitory effect of Na^+ , K^+ , Mg^{2+} , Ca^{2+} on the uptake of Pb^{2+} on equilibrium

followed $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$, and Ca^{2+} had the greatest influence on Pb^{2+} adsorption. Ramalingam et al. [21] found that when the crab shell particles were exposed to the initial concentration of 2,000 mg L^{-1} calcium ($\text{Pb}^{2+} = 100 \text{ mg L}^{-1}$), the adsorption capacity for Pb^{2+} was reduced about 30%. Chatterjee et al. [22] reported that when the concentration of Pb^{2+} fixed in 0.1 mmol L^{-1} while Ca^{2+} varied from 0 to 100 mg L^{-1} , the breakthrough time of Pb^{2+} was reduced from 20 h to 2 h. Since the degree of inhibitory effect on Pb^{2+} adsorption is concerned with the relative initial concentration of co-ions, it is necessary to investigate it in detail to find the optimal condition for separation of Pb^{2+} from wastewater.

In this study, we prepared pyromellitic dianhydride modified SCB to treat the simulated lead-containing waste water under dynamic condition. To determine the optimal condition for Pb^{2+} selective adsorption, Ca^{2+} , as a common co-ion with interference on the adsorption of Pb^{2+} , was chosen as the model interfering ions. Adsorption of Pb^{2+} and Ca^{2+} in single ion component was conducted for comparison. The influence of the initial concentration of Ca^{2+} on Pb^{2+} adsorption was determined by fixing Pb^{2+} concentration and increasing Ca^{2+} concentration. Breakthrough curves of Pb^{2+} on the modified SCB fixed bed column under different initial concentration ratio of Ca^{2+} and Pb^{2+} ($C_0^{\text{Ca}} : C_0^{\text{Pb}}$) were studied. Desorption of Ca^{2+} and Pb^{2+} on the saturated column was studied by using hydrochloric acid as the eluent. According to the elution curve, amounts of Ca^{2+} and Pb^{2+} adsorbed on the column were calculated. The relationship between $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ and the adsorption capacity ratios of the two metal ions ($q_e^{\text{Ca}} : q_e^{\text{Pb}}$) were determined, and the optimum condition for Pb^{2+} removal was concluded. Lastly, the simulated lead-containing waste water containing K^+ , Na^+ , Cd^{2+} and Ca^{2+} was treated.

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MATERIALS AND METHODS

1. Materials

SCB was collected and boiled in water for 40 minutes, and then washed with distilled water three times. After being dried at 60 °C for 24 h, it was ground with a mill and particles between the size of 75 and 150 μm were selected. Pyromellitic dianhydride (PMDA) and other chemicals of reagent grade were purchased from Sino-pharm Chemical Reagent Co. (Shanghai, China). pH of metal solution was adjusted with hydrochloric acid or sodium hydroxide solution.

2. Preparation of Modified Sorbent

A 15.0 g of PMDA and 10.0 g of SCB were added into a round-bottom flask containing 300 mL of N,N-dimethylacetamide [23]. After stirring at 60 °C for 4 h, the modified SCB was obtained, and it was washed in order of NaOH (0.1 M) and distilled water. Then it was dried at 60 °C for 24 h before use.

3. Batch Adsorption Experiment

Isotherm experiment was carried out at room temperature and 120 rpm on an orbital shaker for 24 h. 0.005 g of the modified SCB was added into 20 mL of Pb^{2+} and Ca^{2+} solution with initial concentration ranging from 0.1 to 0.8 mM and 0.05 to 1 mM, respectively, at pH 5.0. The residual concentration of metal ions after adsorption was determined by atomic absorption spectrophotometer. The amounts of metal ions absorbed were calculated by the following equation:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where q_t (mg g^{-1}) is the amount of metal ions adsorbed per unit mass of the sorbent, V (mL) is the sample volume, C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the initial and equilibrium concentration, respectively, and m (g) is the weight of the sorbent. The adsorption isotherms of Pb^{2+} and Ca^{2+} were fitted by Langmuir (Eq. (2)), Freundlich (Eq. (3)) and Temkin (Eq. (4)) equations.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

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

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F ($\text{mmol L}^{-1}/n \text{ g}^{-1} \text{ mg}^{-1}/n$) is a constant representing the adsorption capacity and n is a constant depicting the adsorption intensity and C_e is the equilibrium concentration of ions in the solution (mg L^{-1}).

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (4)$$

where A_T (L mmol^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy, b_T (g mmol^{-1}) is the Temkin isotherm constant, T is the temperature (K), and R is the ideal gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$).

4. Dynamic Adsorption Experiments

The column for these studies was a glass tube ($20 \times 1 \text{ cm}$), and the experiment was conducted at room temperature. A 0.5 g of the modified SCB was accurately weighed and added into 50 mL of distilled water. After ultrasonic dispersion uniformity, the modified SCB was poured slowly into the column. When the adsorbent had settled, the column was pumped with distilled water for 30 min. The peristaltic pump (YZ1515X, Longer pump) was connected with Teflon tubes from the sample tank to the bottom of the column at the designated flow rate (up flow pattern) of 6.25 mL min^{-1} , and then the solutions were pumped to the column with modified SCB. Solution pH in all the experiment was kept at 5.0. The concentration of Pb^{2+} used in the dynamic experiment was all fixed at 0.5 M. In the binary system, mixture solutions of Ca^{2+} and Pb^{2+} with molar concentration ratio of 1:1, 10:1, 20:1, 50:1 and 100:1 were pumped into the fixed bed column. Effluent samples were taken from a sample point (at the top of the column) at regular time intervals, and the concentrations of the metal ions were measured by an atomic adsorption spectrophotometer. The adsorption capacity of the sorbent q_t (mg g^{-1}) was calculated by the following equation (calculated by using the software origin 8.0):

$$q_t = \frac{v \int_{t=0}^{t=t} (C_0 - C_t) dt}{m} \quad (5)$$

5. Dynamic Desorption Experiment

In the desorption experiment of the saturated column, HNO_3 (0.1 M) was taken as eluent, and it was pumped to the column at the flow rate of 4 mL min^{-1} . Concentrations of Pb^{2+} and Ca^{2+} in the eluate at time t (C'_t , mmol L^{-1}) were measured. The amount of metal ions desorbed at time t (q'_t , mg g^{-1}) could be calculated by the following equation (calculated by using the software origin 8.0):

$$q'_t = \frac{v \int_{t=0}^{t=t} (C'_0 - C'_t) dt}{m} \quad (6)$$

6. Treating Simulated Waste Water Experiment

The adsorption behavior of the modified SCB in treating simulated wastewater was studied. The concentrations of K^+ , Na^+ , Cd^{2+} , Ca^{2+} , were all 0.2 mM and that of Pb^{2+} was 0.5 mM. pH of simulated wastewater was 5.0. 0.5 g of modified SCB was fixed in the column and the flow rate was 6.25 mL min^{-1} . After the fixed column was saturated, 0.1 mM hydrochloric acid was used as desorption agent with the flow rate of 4 mL min^{-1} to regenerate the column. Concentrations of Pb^{2+} , K^+ , Na^+ , Cd^{2+} and Ca^{2+} in the eluate at time t (C_t , mM) were measured by an atomic adsorption spectrophotometer. The amount of metal ions desorbed at time t (q_t , mg g^{-1}) could be calculated by Eq. (6) (calculated by using the software origin 8.0).

RESULTS AND DISCUSSION

1. Adsorption of Pb^{2+} on the Modified SCB Fixed Bed Column in One Component System

SEM image of the modified SCB shown in Fig. 1 illustrates that the modified SCB surface was smooth and porous. Breakthrough curves and adsorption capacity of Pb^{2+} on the modified SCB fixed

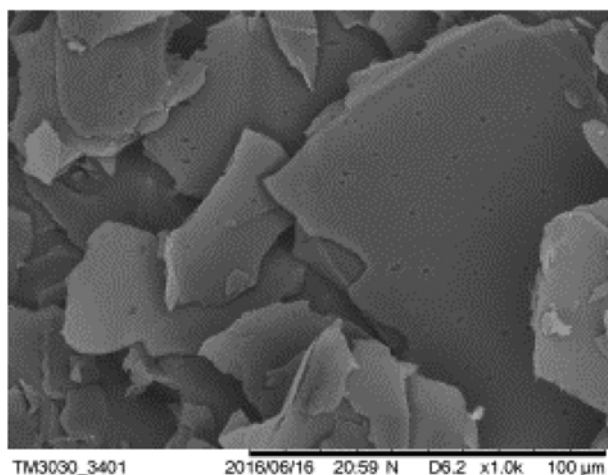
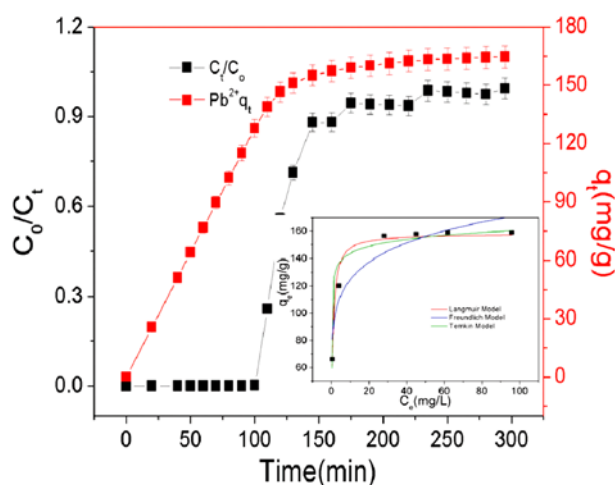


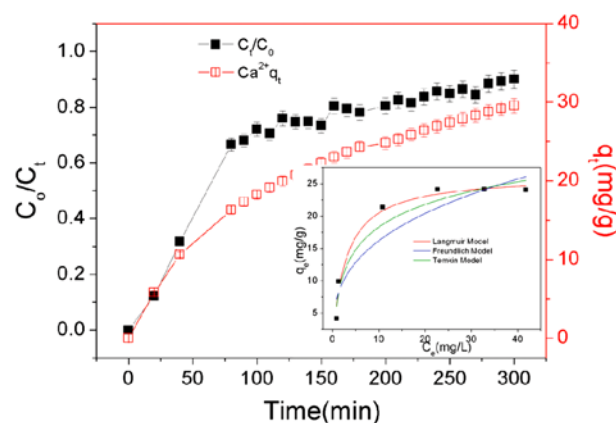
Fig. 1. SEM image of the modified SCB.

Fig. 2. Breakthrough curve (line, left vertical axis) and saturated sorption capacity (line, right vertical axis) of Pb^{2+} on modified SCB fixed bed column at inlet concentration of 0.5 mM. Inset: Adsorption isotherm of Pb^{2+} on modified SCB in single ion solution under batch system (amount of sorbent=0.5 g, flow rate=6.25 mL min⁻¹, pH=5.0).

bed column at the flow rate of 6.25 mL min⁻¹ are shown in Fig. 2. The breakthrough curve presents an obvious “S” shape. C_t/C_0 was much lower than 0.05 and the removal efficiency of Pb^{2+} was higher than 99% before 100 min, demonstrating Pb^{2+} was removed efficiently from the aqueous solution at the beginning of adsorption, which was due to the large amount of unoccupied active sites (carboxyl groups). Part of the Pb^{2+} could not be adsorbed and began to flow out with the occupation of carboxyl groups; thus C_t/C_0 increased sharply to 1.0 after 100 min and adsorption reached equilibrium at 150 min. The amount of Pb^{2+} adsorbed at time t (q_t) was calculated according to Eq. (5) and shown in Fig. 2. It showed that the saturated capacity of the column for Pb^{2+} under this condition was 168.91 mg g⁻¹. For comparison, adsorption capacity of Pb^{2+} was conducted under batch system, and the adsorption isotherm is shown in inset of Fig. 2. The curves are fitted better by Langmuir model than by Freundlich and Temkin models. According

Table 1. Physicochemical property of metal ions

Metal ions	Atomic weight	Covalent radius (nm)	Electronegative	Hydrated ionic radii (nm)
Pb^{2+}	207.2	0.147	2.33	0.401
Ca^{2+}	40.08	0.174	1.0	0.412
K^+	39.10	0.203	0.82	0.331
Na^+	22.99	0.154	0.93	0.358
Cd^{2+}	112.4	0.148	1.69	0.426

Fig. 3. Breakthrough curve (line, left vertical axis) and saturated sorption capacity (line, right vertical axis) of Ca^{2+} on modified SCB fixed bed column at inlet concentration of 0.5 mM. Inset: Adsorption isotherm of Ca^{2+} on modified SCB in single ion solution under batch system (amount of sorbent=0.5 g, flow rate=6.25 mL min⁻¹, pH=5.0).

to the Langmuir model, the adsorption capacity for Pb^{2+} was 157.05 mg g⁻¹, which was very close to that obtained in this experiment. Similar results were reported by Yu et al. [24].

2. Adsorption of Ca^{2+} on the Modified SCB Fixed Bed Column in One-component System

Different from Pb^{2+} , the breakthrough curve of Ca^{2+} was not in the shape of an “S”, and C_t/C_0 increased sharply at the beginning of the adsorption, then the tendency became gentle till equilibrium at 270 min. The difference between Pb^{2+} and Ca^{2+} presented by breakthrough curves was due to the different adsorption affinity, which was ascribed to the fact that Pb^{2+} has the larger atomic weight (207.2), more electronegative (Pb:2.33 and Ca:1.0) and smaller hydrated ionic radii (Pb:0.401 nm and Ca:0.412 nm). The physicochemical properties of Pb^{2+} and Ca^{2+} and other metal ions are shown in Table 1. The amount of Ca^{2+} adsorbed at time t (q_t) was calculated and shown in Fig. 3. The saturated capacity of the column for Ca^{2+} under this condition was 29.86 mg g⁻¹, which was close to that (24.65 mg g⁻¹) obtained in the batch system (shown in inset of Fig. 3).

3. Effects of Initial Concentration Ratio on Adsorption of Pb^{2+} on the Modified SCB Fixed Bed Column in the Binary System

To investigate the effect of Ca^{2+} concentration on the adsorption of Pb^{2+} , experiments were carried out at different initial mole concentration ratios ($C_0^{\text{Ca}} : C_0^{\text{Pb}}$) on the fixed bed column. Fig. 4(a) and 4(b) show the breakthrough curves and adsorption kinetic of

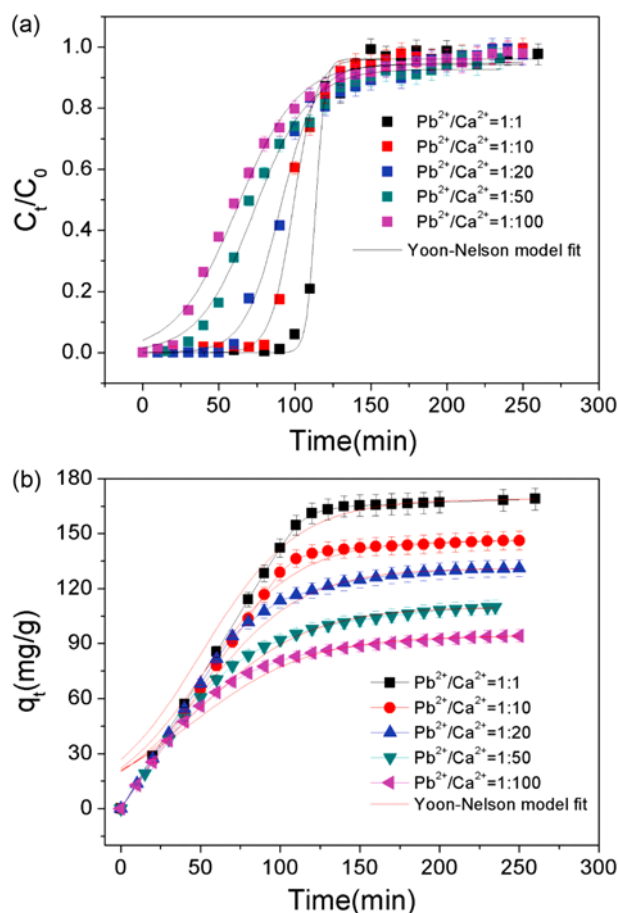


Fig. 4. (a) Breakthrough curves and (b) dynamic adsorption kinetic of Pb^{2+} on the fixed-bed column at different $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ (amount of sorbent = 0.5 g, inlet concentration of Pb^{2+} = 0.5 mM, flow rate = 6.25 mL min⁻¹, pH = 5.0).

Pb^{2+} on the modified SCB fixed bed column. It was observed that breakthrough curves were dispersed and breakthrough occurred faster at high $C_0^{\text{Ca}} : C_0^{\text{Pb}}$. Breakthrough time ($C_t/C_0 = 0.05$) of Pb^{2+} decreased obviously from 105 to 91, 78, 21 and 5 min when $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ increased from 1 : 1 to 10 : 1, 20 : 1, 50 : 1 and 100 : 1, and the amount

of Pb^{2+} absorbed decreased from 168.54 to 146.26, 131.05, 109.89 and 94.26 mg g⁻¹, respectively. The decrease in breakthrough time and adsorption capacity for Pb^{2+} was ascribed to the competitive inhibition effect caused by Ca^{2+} . Similar results were reported by Al-Masri et al. [25] and Yin et al. [26]. Both of the two metals compete for the same active sites, and their adsorption was decided by the affinity order, initial concentration ratio and pH. High concentration of Ca^{2+} would hinder the adsorption of Pb^{2+} while promote the adsorption of Ca^{2+} on the column.

With the aim of describing the fixed bed column behavior, the breakthrough curves of Pb^{2+} at different molar ratios were fitted by Yoon-Nelson model nonlinear curve regressive analysis (Eq. (7)).

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp[-k_{YN}(t - \tau)]} \quad (7)$$

The fitted results in Table 2 show that the calculated values of τ for Pb^{2+} were 113.71, 98.96, 90.30, 73.09, and 61.90 min, individually, at different concentration ratios, which were very close to the experimental values. Since all the breakthrough curves matched the Yoon-Nelson model well, the attempt to find the relationship between q_t and time t was tried by using a modified Yoon-Nelson model (Eq. (8)); the results are shown in Table 2.

$$q_t = \frac{q_m}{1 + \exp[-k_{YN}(t - \tau)]} \quad (8)$$

Calculated q_m at $C_0^{\text{Ca}} : C_0^{\text{Pb}} = 1 : 1, 10 : 1, 20 : 1, 50 : 1$ and $100 : 1$ were 168.57, 145.34, 127.76, 106.02, and 90.81 mg g⁻¹, which matched the experimental results 168.54, 146.26, 131.05, 109.89 and 94.26 mg g⁻¹ well, demonstrating the availability of the modified Yoon-Nelson model.

4. Desorption of Pb^{2+} and Ca^{2+} from the Saturated Fixed Bed Column Obtained at Different Initial Concentration Ratio of the Two Metal Ions

To confirm the adsorption capacity of Pb^{2+} and determine the amount of Ca^{2+} loaded on the saturated fixed bed, hydrochloric acid (0.1 M) was chosen as eluent solution for the desorption experiment. Elution curves of the two metal ions that deviated from saturated column obtained at different ratios of $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ are shown

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

Concentration ratio $C_0^{\text{Ca}} : C_0^{\text{Pb}}$	K_{YN} (min ⁻¹)	τ (min)	R^2	$\Sigma[(C_t/C_0)_{\text{exp}} - (C_t/C_0)_{\text{cal}}]^2$
1 : 1	0.332 ± 0.04	113.71 ± 0.58	0.99	0.02
10 : 1	0.133 ± 0.01	98.96 ± 0.07	0.99	0.03
20 : 1	0.085 ± 0.01	90.30 ± 1.38	0.99	0.04
50 : 1	0.055 ± 4 × 10 ⁻³	73.09 ± 1.48	0.99	0.03
100 : 1	0.050 ± 3 × 10 ⁻³	61.90 ± 1.32	0.99	0.02
Concentration ratio $C_0^{\text{Ca}} : C_0^{\text{Pb}}$	K'_{YN} (min ⁻¹)	τ' (min)	R^2	q_m (mg g ⁻¹)
1 : 1	0.043 ± 2 × 10 ⁻³	59.74 ± 1.38	0.99	168.57 ± 1.51
10 : 1	0.044 ± 2 × 10 ⁻³	56.46 ± 0.95	0.99	145.34 ± 0.94
20 : 1	0.046 ± 2 × 10 ⁻³	48.93 ± 1.22	0.99	127.76 ± 1.08
50 : 1	0.042 ± 2 × 10 ⁻³	46.77 ± 1.73	0.98	106.02 ± 1.73
100 : 1	0.044 ± 2 × 10 ⁻³	42.70 ± 1.72	0.98	90.81 ± 1.06

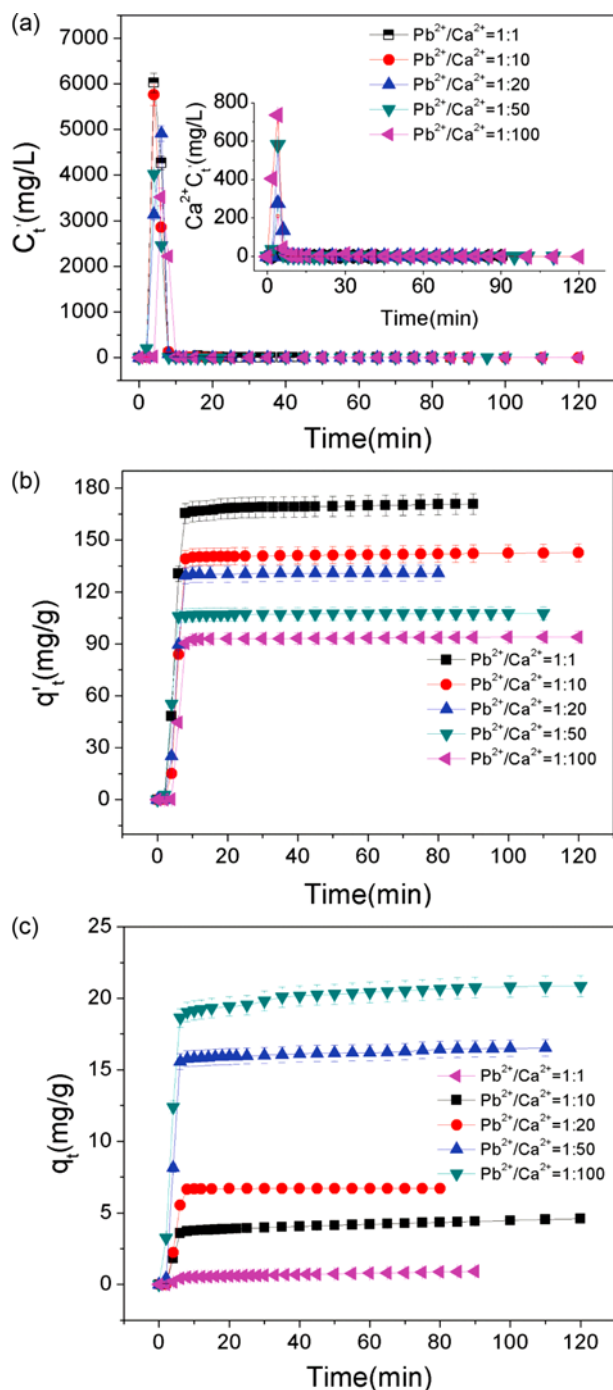


Fig. 5. (a) Elution curves of Pb^{2+} and Ca^{2+} , and desorption kinetics of (b) Pb^{2+} and (c) Ca^{2+} on the saturated column obtained at different $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ (amount of sorbent=0.5 g, inlet concentration of hydrochloric acid=0.1 mM, flow rate=6.25 mL min⁻¹).

in Fig. 5(a). It is obvious that the concentration of Pb^{2+} and Ca^{2+} increased suddenly at first; after 8 min almost all ions desorbed from the column and equilibrium was attained. When $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ increased from 1:1 to 10:1, 20:1, 50:1 and 100:1, the maximum concentration of Pb^{2+} in the eluate was decreased from 6,022.43 to 5,756.99, 4,908.78, 4,015.95 and 3,521.80 mg L⁻¹, while that of Ca^{2+} increased from 22.76 to 209.85, 276.91, 582.85 and 736.32 mg L⁻¹,

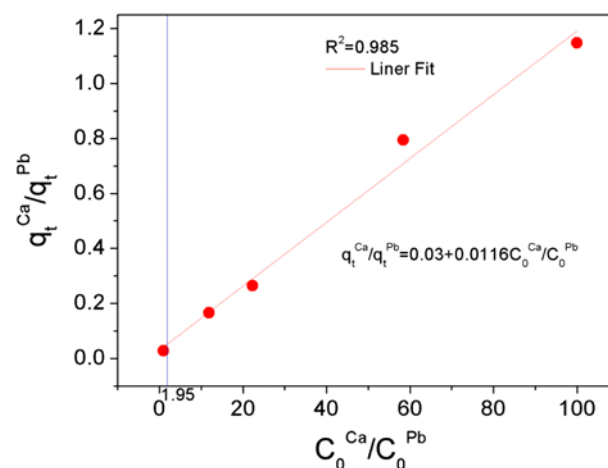


Fig. 6. Linear relationship between the initial concentration of Ca^{2+} and Pb^{2+} and their adsorption capacity on modified SCB.

respectively. Desorption amount (q_t) of Pb^{2+} and Ca^{2+} at different ratios of $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ was calculated and shown in Fig. 5(b) and 5(c). q_e^{Pb} was 170.77, 142.68, 130.79, 107.61 and 93.98 mg g⁻¹, and q_e^{Ca} was 0.93, 4.59, 6.70, 16.53 and 20.85 mg g⁻¹ when $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ increased from 1:1 to 10:1, 20:1, 50:1 and 100:1. From the results obtained, it was found apparently that adsorption amount of Pb^{2+} decreased while Ca^{2+} increased with the increase of $C_0^{\text{Ca}} : C_0^{\text{Pb}}$, which opened a way to verify the initial concentration ratio had a significant influence on the adsorption of the two metal ions. Since q_e^{Pb} decreased while q_e^{Ca} increased with the increasing of $C_0^{\text{Ca}} : C_0^{\text{Pb}}$, the relationship between $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ and $q_e^{\text{Ca}} : q_e^{\text{Pb}}$ was tried to be determined. Fig. 6 shows a good linear relationship between $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ and $q_e^{\text{Ca}} : q_e^{\text{Pb}}$ was observed (Eq. (9)). Similar result was reported by Yu et al. [27].

$$q_t^{\text{Ca}} / q_t^{\text{Pb}} = 0.03 + 0.0116 C_0^{\text{Ca}} / C_0^{\text{Pb}} \quad (9)$$

Ordinarily, when mass ratio of Pb^{2+} on the modified SCB is higher than 95%, Pb^{2+} is deemed to be removed by the fixed column selectively, which also can be applied to Ca^{2+} . By using Eq. (5), mass ratio of Pb^{2+} and Ca^{2+} at different initial concentration ratio could be calculated, and it was found that mass ratio was higher than 95% for Pb^{2+} at $C_0^{\text{Ca}} / C_0^{\text{Pb}} < 1.95$ and for Ca^{2+} $C_0^{\text{Ca}} / C_0^{\text{Pb}} > 1635.34$, respectively. The two ions can be separated directly by the modified SCB fixed bed column when the initial concentration ratio was at $C_0^{\text{Ca}} / C_0^{\text{Pb}} < 1.95$ or $C_0^{\text{Ca}} / C_0^{\text{Pb}} > 1635.34$ (shown in the inset of Fig. 6).

Since Pb^{2+} could be selectively adsorbed from the mixture solution at $C_0^{\text{Ca}} / C_0^{\text{Pb}} < 1.95$, it was necessary to make the selective adsorption mechanism clear. Take $C_0^{\text{Ca}} : C_0^{\text{Pb}} = 1:1$ for example, the breakthrough curves and adsorption kinetics of Pb^{2+} and Ca^{2+} on the column are shown in Fig. 7(a) and Fig. 7(b). Fig. 6(a) shows that the breakthrough curves of Pb^{2+} and Ca^{2+} differed considerably. For Pb^{2+} , C_t / C_0 increased steadily after 95 min until it reached the equilibrium point at 140 min, and Pb^{2+} was removed completely from aqueous before 95 min. For Ca^{2+} , C_t / C_0 increased sharply from 0.0 to 1.0 before 25 min, and overshoot the normal maximum dimensionless value of 1.0 during the time from 25 to 145 min. The higher values of C_t than C_0 demonstrated that the

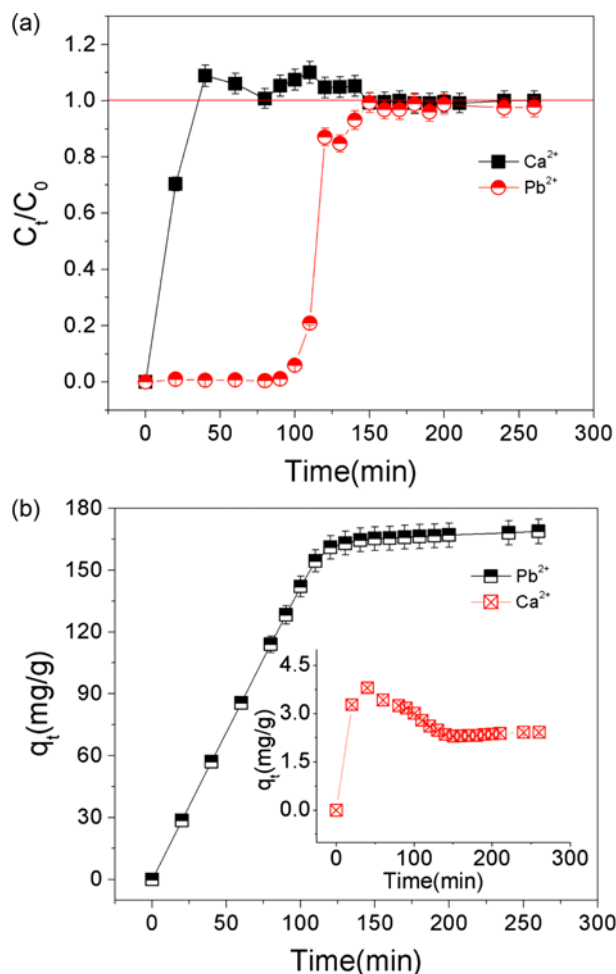


Fig. 7. (a) Breakthrough curves of Pb^{2+} and Ca^{2+} and (b) amount of Pb^{2+} adsorbed on the fixed-bed column. Inset: Amount of Ca^{2+} adsorbed on the fixed-bed column (amount of sorbent = 0.5 g, inlet concentration of Pb^{2+} = 0.5 mM, Ca^{2+} = 0.5 mM, flow rate = 6.25 mL min⁻¹, pH = 5.0).

up-loaded Ca^{2+} was desorbed and released from the sorbent surface into the aqueous solution. Fig. 6(b) shows the adsorption kinetics of Pb^{2+} and Ca^{2+} on the modified SCB. It was observed that the adsorbed amount of Pb^{2+} increased with the time passing till equilibrium (167.5 mg g⁻¹), while that of Ca^{2+} increased at first to a maximum of 4.3 mg g⁻¹ and then decreased to the equilibrium value of 2.0 mg g⁻¹. About 2.3 mg g⁻¹ of Ca^{2+} was pushed off from the sorbent surface, which was ascribed to the competitive substitution reaction between Pb^{2+} (high adsorption affinity) and Ca^{2+} (low adsorption affinity). Substitution reaction induced by the different adsorption affinity led to the selective adsorption of Pb^{2+} from the mixture solution by the modified SCB.

5. Treating Simulated Waste Water

The adsorption behavior of simulated water treated by modified SCB fixed bed column was studied. Breakthrough curves of Pb^{2+} , K^+ , Na^+ , Cd^{2+} , Ca^{2+} in the simulated waste water are shown in Fig. 8(a). It is obvious that different ions present different adsorption behaviors. For Pb^{2+} , the breakthrough curve was very similar to that in binary and unitary system, and breakthrough time and sat-

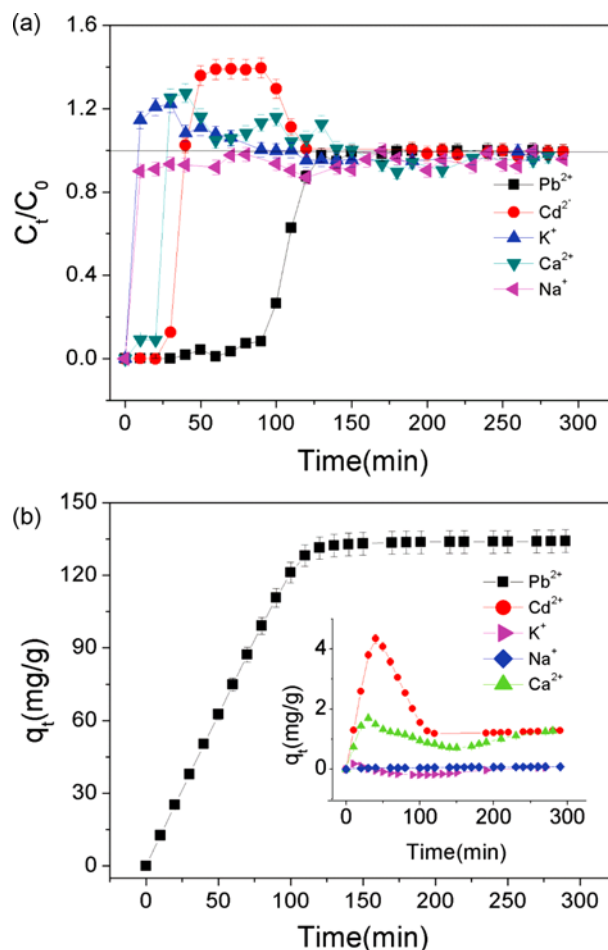


Fig. 8. (a) Breakthrough curves of Pb^{2+} , K^+ , Na^+ , Cd^{2+} and Ca^{2+} and (b) dynamic adsorption kinetic of Pb^{2+} on the fixed-bed column. (b) Inset: Dynamic adsorption kinetic of K^+ , Na^+ , Cd^{2+} and Ca^{2+} (amount of sorbent = 0.5 g, flow rate = 6.25 mL min⁻¹, pH = 5.0).

urated time were 75 and 130 min, respectively. For K^+ , Ca^{2+} , C_t/C_0 overshoot directly from 0 to 1.14 and 1.25, respectively. For Cd^{2+} , C_t/C_0 increased to 1.0 at 40 min, and then overshoot to 1.35 at 50 min. For Na^+ , C_t/C_0 increased to 1.0 at the beginning, and it did not overshoot in the whole process. The above phenomena demonstrated an apparent competitive substitution reaction happened in the adsorption process. At the beginning of adsorption process, there were many unoccupied active sites on the surface of the modified SCB, and parts of K^+ , Ca^{2+} and Cd^{2+} were adsorbed onto it. With the occupation of the available sites, the adsorbed metal ions including K^+ , Ca^{2+} and Cd^{2+} were replaced by Pb^{2+} and released into the aqueous solution. The column reached equilibrium at 200 min.

The amount of metal ions adsorbed on the fixed bed column at time t (q_t , mg g⁻¹) was calculated and shown in Fig. 8(b). The maximum adsorption amount of Na^+ was 0.083 mg g⁻¹. For K^+ , Cd^{2+} , Ca^{2+} , at the beginning of adsorption process, q_t increased to the maximum values of 0.18, 4.34, 1.69 mg g⁻¹, and then decreased to equilibrium values of 0.058, 1.28, 1.28 mg g⁻¹, respectively. Thus, about 0.122 mg g⁻¹ of K^+ , 3.06 mg g⁻¹ of Cd^{2+} , 0.41 mg g⁻¹ of Ca^{2+} were replaced during this process. For Pb^{2+} , the value of q_t increased

steadily to 134.14 mg g^{-1} till adsorption equilibrium was obtained. The equilibrium amount of Pb^{2+} , Na^+ , K^+ , Cd^{2+} , Ca^{2+} and adsorbed at the column were 134.14 , 0.083 , 0.058 , 1.28 , and 1.28 mg g^{-1} , respectively, demonstrating that the modified SCB fixed bed column could selectively adsorb Pb^{2+} from the simulated lead-containing waste water.

CONCLUSIONS

Pyromellitic dianhydride modified SCB was prepared and used to adsorb Pb^{2+} from aqueous solution under dynamic condition. Results showed that q_e^{Pb} and q_e^{Ca} in the unitary system were 168.91 mg g^{-1} and 29.86 mg g^{-1} , respectively. q_e^{Pb} decreased to 168.54 , 146.26 , 131.05 , 109.89 and 94.26 mg g^{-1} while q_e^{Ca} increased to 0.93 , 4.59 , 6.70 , 16.53 and 20.85 mg g^{-1} when $C_0^{\text{Ca}} : C_0^{\text{Pb}}$ increased from $1 : 1$ to $10 : 1$, $20 : 1$, $50 : 1$ and $100 : 1$ in the binary system. Initial concentration ratio played a key role on the adsorption of the two metal ions. It was found that $q_e^{\text{Ca}} : q_e^{\text{Pb}}$ increased linearly with the increase of $C_0^{\text{Ca}} : C_0^{\text{Pb}}$, and the optimal condition for Pb^{2+} selective removal was concluded to $C_0^{\text{Ca}}/C_0^{\text{Pb}} < 1.95$. In this concentration range, weight percentage of Pb^{2+} in the eluate was higher than 95%. The modified SCB could be used to remove Pb^{2+} from the simulated waste water containing K^+ , Na^+ , Cd^{2+} and Ca^{2+} with initial concentration of each ion 0.2 mM .

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NOMENCLATURE

C_0	: the inlet concentration of metal ion [mmol L^{-1}]
C_t	: the concentration of metal ion in the effluent at time t [mmol L^{-1}]
C'_t	: concentrations of metal ions in the eluate at time t [mmol L^{-1}]
K_{YN}	: rate constant of Yoon-Nelson model [min^{-1}]
K'_{YN}	: rate constant of modified Yoon-Nelson model [min^{-1}]
m	: the mass of the modified SCB settled in the fixed bed column [g]
q_t	: the amount of metal ions desorbed at time t [mg g^{-1}]
q'_t	: desorption amount [mg g^{-1}]
q_e	: mass of metal ions adsorbed at equilibrium [mg g^{-1}]
q_m	: the calculated adsorption capacity of the sorbent in the dynamic system [mg g^{-1}]
R^2	: correlation coefficient

τ	: adsorption constants in Yoon-Nelson model, the time required for reaching 50% adsorbate breakthrough [min]
τ'	: adsorption constants in modified Yoon-Nelson model
t	: time [min]
v	: the volumetric flow rate [mL min^{-1}]

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