Novel magnetic beads based on sodium alginate gel crosslinked by zirconium(IV) and their effective removal for Pb$^{2+}$ in aqueous solutions by using a batch and continuous systems

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ABSTRACT

Novel magnetic sodium alginate gel beads (Fe$_3$O$_4$@SA–Zr) were successfully prepared by using zirconium(IV) as crosslinking ions, and used as adsorbent for removal of Pb$^{2+}$ ions from aqueous solutions in batch and fixed-bed column systems. Fe$_3$O$_4$@SA–Zr had the macroporous structure, exhibited greater stability and possessed a sensitive magnetic response. More importantly, Fe$_3$O$_4$@SA–Zr exhibited high adsorption capacity, fast kinetics and high selectivity towards Pb$^{2+}$ ions. Experimental data was well described by Langmuir isotherm with a maximum adsorption capacity of 333.33 mg/g. FTIR and XPS indicated that the carboxyl and hydroxyl groups of SA and hydroxyl groups binding to Fe and Zr species were involved in Pb$^{2+}$ adsorption. Fixed-bed column packed with Fe$_3$O$_4$@SA–Zr exhibited higher removal efficiency for Pb$^{2+}$ ions. Consequently, Fe$_3$O$_4$@SA–Zr with excellent absorbability, stability and reusability could be used as a promising adsorbent for Pb$^{2+}$ removal in wastewaters.

1. Introduction

Wastewater containing heavy metals such as lead, cadmium, mercury, chromium, copper, etc., discharged from various industrial activities is becoming a serious global environmental problem facing man. Their presence in the aquatic ecosystem causes harmful effects to living organisms because these heavy metals are not biodegradable and can be accumulated through the food chain. Thus, the removal of heavy metals is very important for the protection of ecological environment and public health. In the last decade, adsorption has been considered as one of the most efficient and promising technologies for the removal of heavy metals from aqueous solutions due to its simplicity, ease in operation, relative low-cost, no sludge generation and low chemicals and energy consumption. Different kinds of adsorbents such as activated carbon (Lima et al., 2011), clay minerals (Ghayaza et al., 2011), metallic oxides (Chen et al., 2012; Zheng et al., 2012), functionalized silica (Li et al., 2011a), resins (Liu et al., 2011), biological adsorbents (Bhatnagar and Sillanpää 2010; Yin et al., 2013), etc., have been investigated their potential for the removal of heavy metals from wastewaters. However, it seems to be difficult to reduce the concentration of heavy metals to the environmentally acceptable level.

In recent years, increased attention has been focused on the investigation of biological materials as adsorbents for removing pollutants, which can reduce total operation cost greatly and make the adsorption technology more environmentally friendly and technically feasible. Sodium alginate, the salt of alginic acid, have already been investigated as adsorbents for the removal of organic and inorganic pollutants from wastewaters due to biodegradability, hydrophilicity, presence of carboxyl and hydroxyl groups, low
cost, natural and renewable nature. Ionic crosslinking can take place when the monovalent sodium ions are replaced by multiva-

telent metal ions and form a gel matrix. Ca\textsuperscript{2+} was the most common crosslinking ions and ionic exchange between Ca\textsuperscript{2+} and metal cat-

tions was the main mechanism for the removal of metal ions (Ngomsik et al., 2006; Maxim et al., 2008). However, Ca–alginate beads are unstable because the replacement of Ca\textsuperscript{2+} ions with H\textsuperscript{+} ions in acidic environment and desorption operation can disinte-
grate the gel matrix and decrease the performances (Jiang et al., 2012; Idris et al., 2011; Rangsayatorn et al., 2004; Lim et al.,

2009). Thus, to enhance the stability, adsorption ability and reus-

ability, other metal ions were used as the crosslinking ions or the doped ions. Min and Hering (1998) prepared Ca\textsuperscript{2+}, Cu\textsuperscript{2+}, Fe\textsuperscript{3+},

and Ca\textsuperscript{2+}–Fe\textsuperscript{3+}-doped alginate gels and they found that Fe beads were easier to crack and peel at the surface, while Ca–Fe beads showed good mechanical stability. Among the beads prepared, Ca–Fe beads showed a significant As(V) sorption compared with Cu and Ca beads, but Fe leaching decreased As(V) sorption at acidic pH. Rosales et al. (2012) evaluated Fe alginate gel beads for deco-

courization of Lissamine Green B and Azure B under electro-Fenton process. They noted that pH affected dye decolourisation rate and the time to obtain the maximum dye decolourisation increased with increase in successive cycles. Niu et al. (2012) noted that core/shell alginate–Fe\textsuperscript{3+}/Fe\textsuperscript{2+} polymer coated Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles removed 100% of NOF within 60 min and F element in NOF molecule changed into F\textsuperscript{−} ions within 1 min. They also found that the dissolved Fe ions from Fe\textsubscript{3}O\textsubscript{4}/ALG/Fe were lower than 0.1 mg/L at pH 3.5.

However, some prepared adsorbents still have some drawbacks, such as complicated preparation, low adsorption capacity and selectivity, long equilibrium time, poor stability and mechanical strength, small particle size, difficult separation and recycling, etc., which make them difficult to use in both batch and continuous operations. Moreover, most studies focused on the batch adsorption experiments whereas the practical applications of large-scale adsorption operation involve the use of continuous flow systems. Therefore, there is a need to develop simple, economic and effective method for the preparation of new adsorption materials with excellent properties such as high adsorption capacity and selectivity, rapid adsorption kinetics, convenient separation, excellent stability and reusability, especially have good column operation properties.

In the present study, Zr(IV) was chosen as the crosslinking ions and the introduction of zirconium not only makes the prepared materials more stable but also improves the adsorption perfor-

dences. This is because tetravalent zirconium ion is easily hydro-

dyzed even at very low concentration to form tetrancular ions or octanuclear species, resulting in a large number of hydroxyl ions and water molecules, which can take part in the ligand exchange reaction with the target pollutants. Balaji et al. (2005) studied the adsorption performance of As(V) and As(III) onto Zr-loaded ly-
sine diacetic acid chelating resin and column studies showed that the adsorption of As(V) is more favorable than that of As(III). Perá

niemi et al. (1994) found that zirconium–loaded activated charcoal was an effective adsorbent for the recovery of As, Se and Hg from aqueous solutions.

In the present study, novel magnetic sodium alginate–zirconium(IV) composite beads (Fe\textsubscript{3}O\textsubscript{4}@SA–Zr) were prepared by using Zr(IV) as the crosslinking ions. There is no report on the removal of heavy metal ions by sodium alginate gel beads using Zr(IV) as the crosslinking ions by far. Compared with the traditional centrifugation or filtration, magnetic separation has become a clean and promising separation technique. The introduction of Fe\textsubscript{3}O\textsubscript{4} would enable Fe\textsubscript{3}O\textsubscript{4}@SA–Zr to be separated easily and rapidly from the reaction system by an external magnetic field and enhance the reusability of the polymer beads. In addition, Fe\textsubscript{3}O\textsubscript{4} has adsorption ability due to its high surface area and the presence of surface hy-
droxygul groups (Nethaji et al., 2013). So the prepared Fe\textsubscript{3}O\textsubscript{4}@SA–Zr polymer beads are expected to possess the enhanced stability and exhibit excellent adsorption performances. Fe\textsubscript{3}O\textsubscript{4}@SA–Zr was char-

acterized by using FTIR, XRD, SEM, VSM and XPS. Pb\textsuperscript{2+}, one of the most toxic heavy metals, was selected as model heavy metal ion. To study the adsorption performances of Fe\textsubscript{3}O\textsubscript{4}@SA–Zr for Pb\textsuperscript{2+} ions, batch adsorption experiments were carried out to examine the effects of solution pH, initial metal concentration, temperature, contact time, ionic strength, humic acid and competitive ions. Adsorption behaviors of Fe\textsubscript{3}O\textsubscript{4}@SA–Zr were analyzed by fitting var-

ious isotherms and kinetic models and thermodynamic parameters were also calculated. FTIR and XPS were used to analyze the interaction of Pb\textsuperscript{2+} ions and Fe\textsubscript{3}O\textsubscript{4}@SA–Zr. The potential of Fe\textsubscript{3}O\textsubscript{4}@SA–Zr in practical applications for Pb\textsuperscript{2+} removal was further studied in continuous flow fixed-bed column at different flow rates and influ-

ent Pb\textsuperscript{2+} concentrations. Additionally, 10 adsorption–desorption cycles were carried out to evaluate the reusability of the new adsorbent.

2. Methods

2.1. Chemicals and materials

Sodium alginate (SA) with a viscosity of 0.02 Pa s in 1% aqueous solution at 20 °C was purchased from Shanghai chemical reagent co., Ltd. (Shanghai, China). Stock solutions of Pb\textsuperscript{2+} (1000 mg/L) were prepared by dissolving an accurately weighed amount Pb(NO\textsubscript{3})\textsubscript{2} in distilled water and then diluted to the desired concentra-
tions ranging from 50 to 800 mg/L. FeCl\textsubscript{3}·6H\textsubscript{2}O, FeCl\textsubscript{2}·4H\textsubscript{2}O, ZrOCl\textsubscript{2}·8H\textsubscript{2}O, NaCl, CaCl\textsubscript{2}, Cu(NO\textsubscript{3})\textsubscript{2}, Cd(NO\textsubscript{3})\textsubscript{2}, HgCl\textsubscript{2}, Zn(NO\textsubscript{3})\textsubscript{2}, humic acid (HA) and all other chemicals used in this work were of analytical grade and used without further purification.

2.2. Preparation of Fe\textsubscript{3}O\textsubscript{4}@SA–Zr polymer beads

Fe\textsubscript{3}O\textsubscript{4} were prepared by the chemical co-precipitation method. Briefly, FeCl\textsubscript{3}·6H\textsubscript{2}O (0.04 mol) were dissolved into 50 mL of dis-
tilled water and stirred under N\textsubscript{2} protection for 30 min. FeCl\textsubscript{2}·4H\textsubscript{2}O (0.02 mol) dissolved into 50 mL of distilled water were added into the above solution. Then 50 mL of NaOH (10 M) were added drop-
wise into the reaction solution. The mixture was stirred for 60 min and heated to 90 °C for another 2 h. The obtained Fe\textsubscript{3}O\textsubscript{4} were se-
parated from solution by a powerful magnet, washed with distilled water, ethanol and acetone, and then dried in an oven at 40 °C. Fe\textsubscript{3}O\textsubscript{4}@SA–Zr polymer beads were prepared as follows: SA (5.0 g) was added into 100 mL of distilled water with constant stir-
ring at room temperature. Fe\textsubscript{3}O\textsubscript{4} (1.0 g) was dispersed in 30 mL of distilled water, kept in an ultrasonic bath for 10 min and then added into the SA solution. The obtained mixture was ultrasonicat-
ced for 30 min and stirred for 6 h at room temperature to obtain a homogeneous mixture. The obtained products were added drop-
wise into 0.1 M Zr(IV) aqueous solution using a syringe. Magnetic alginate droplets were precipitated to form spherical gel beads in Zr(IV) solution due to the ionic crosslinking between carboxyl groups of SA and Zr(IV) ions. These composite beads were allowed to harden for 24 h in the gelling solution, washed thoroughly with distilled water and then stored in distilled water for the adsorption study.

2.3. Characterization of Fe\textsubscript{3}O\textsubscript{4}@SA–Zr

The wet Fe\textsubscript{3}O\textsubscript{4}@SA–Zr was frozen in liquid nitrogen and freeze-dried. The freeze-dried samples were used for analysis. The morphological structure of Fe\textsubscript{3}O\textsubscript{4}@SA–Zr was examined by
using a scanning electron microscope (SEM, HITACHI S-4800). The functional groups of SA, Fe$_3$O$_4$@SA–Zr before and after Pb$^{2+}$ adsorption were analyzed by Fourier transform infrared spectroscopy (FTIR, NEXUS 670, Nicolet, USA). X-ray diffraction (XRD) spectrum of Fe$_3$O$_4$@SA–Zr was performed using a D8 Advance X-ray diffraction spectrometer (Bruker, Germany). Magnetization measurements were performed using a vibrating sample magnetometer (VSM, Lakeshore 7304). The chemical analysis for the virgin and Pb$^{2+}$-loaded Fe$_3$O$_4$@SA–Zr were conducted by X-ray photoelectron spectroscopy (XPS, ESCALAB210, VG, UK). The concentration of metal ions in the solution was determined by using an inductively coupled plasma spectrometer (ICP/IRIS Advantage, Thermo, America).

### 2.4. Batch adsorption studies

Batch adsorption experiments were conducted in 100 mL stopper conical flasks and shaken on a temperature controlled shaker at 120 rpm for 24 h. The effect of solution pH was investigated by varying the initial pH from 1.0 to 6.0 with the adsorbent dosage of 2 g/L and initial Pb$^{2+}$ concentration of 100 mg/L. The effect of initial Pb$^{2+}$ concentration was carried out by varying the initial Pb$^{2+}$ concentrations from 50 to 800 mg/L with the adsorbent dosage of 2 g/L and solution pH of 5.0. The effect of temperature on adsorption behaviors was performed at the temperature in the range of 20–40 °C at adsorbent dosage of 2 g/L and solution pH of 5.0. The effect of contact time on adsorption was carried out at adsorbent dosage of 2 g/L, initial Pb$^{2+}$ ions concentration of 50–400 mg/L, solution pH of 5.0. The effect of ionic strength on adsorption performance was conducted using NaCl and CaCl$_2$ as the ionic medium in the range of 0.005–0.1 mol/L with the adsorbent dosage of 2 g/L at an initial Pb$^{2+}$ concentration of 100 mg/L. The effect of natural organic matter such as HA was carried out by varying HA concentration in the range of 2–20 mg/L.

The adsorption capacity ($Q_e$) and removal percentage (R%) of Pb$^{2+}$ by Fe$_3$O$_4$@SA–Zr at the equilibrium can be calculated by:

\[
Q_e = \frac{(C_0 - C_e)V}{W}
\]

(1)

\[
R(\%) = \frac{C_0 - C_e}{C_0} \times 100\%
\]

(2)

where $C_0$ and $C_e$ are the initial and equilibrium metal concentrations in solution (mg/L), respectively. $V$ is the solution volume (L) and $W$ is the mass of adsorbent (g).

### 2.5. Column adsorption studies

The fixed-bed column operation was conducted in a glass column having a length of 40 cm and an internal diameter of 2.0 cm. Some glass beads were kept at the bottom and top of the column to stabilize the polymer beads in the column. Metal solutions of a known concentration was pumped downward using a peristaltic pump at a fixed flow rate to the column packed with Fe$_3$O$_4$@SA–Zr at a bed height of 7.5 cm. The samples were collected at different intervals from the effluent and were analyzed until the concentration of Pb$^{2+}$ in the effluent was equal to that in the influent. All the adsorption experiments were performed in triplicate and the average value was used.

### 3. Results and discussion

#### 3.1. Characterization of Fe$_3$O$_4$@SA–Zr beads

When magnetic alginate droplets were dripped into Zr(IV) aqueous solution, ionic crosslinking took place between the carboxyl groups of alginate chains and Zr(IV). Since Ca$^{2+}$ can crosslink ionically with two carboxyl groups of SA to form an “egg-box” structure (Shi et al., 2005), Fe$^{3+}$ can crosslink ionically with three carboxyl groups of SA (Min and Hering, 1998), while tetravalent Zr$^{4+}$ ions may crosslink ionically with two, three or even four carboxyl groups to form a three-dimensional bonding structure, as shown in Supplementary Fig. S1. Thus, this three-dimensional bonding structure would endow the Fe$_3$O$_4$@SA–Zr beads with the enhanced stability. It can be seen that Fe$_3$O$_4$@SA–Zr was not a perfect spherical shape with an average diameter of about 2.4 mm (Supplementary Fig. S2a). The outer surface of Fe$_3$O$_4$@SA–Zr was rough and corrugated with many cavities (Supplementary Fig. S2b). Supplementary Fig. S2c and d showed the cross-section structure and morphology of the Fe$_3$O$_4$@SA–Zr. Fe$_3$O$_4$@SA–Zr showed highly porous structure, these pores were interconnected and heterogeneous with different sizes, which may be caused by the nonuniform crosslinking between Zr$^{4+}$ and carboxyl groups of SA throughout the polymer beads. Obviously, the rough surface, macroporous and macroreticular structure of Fe$_3$O$_4$@SA–Zr would provide more active sites for metal ions binding and enhance the mass transfer of metal ions into the interior of the beads and correspondingly improve the adsorption capacity and adsorption rate. More importantly, the prepared Fe$_3$O$_4$@SA–Zr exhibited the spherical shape, favouring to be used in the continuous flow fixed-bed column operation.

FTIR spectra of SA, Fe$_3$O$_4$@SA–Zr and Pb$^{2+}$-loaded Fe$_3$O$_4$@SA–Zr were shown in Supplementary Fig. S3a. For FTIR spectrum of SA, two bands at around 3431.9 and 1034.0 cm$^{-1}$ were attributed to –OH and C–O stretching vibrations, respectively, indicating the presence of hydroxyl groups. While two peaks at 1612.1 and 1418.4 cm$^{-1}$ corresponding to C=O asymmetric and symmetric stretching vibrations of the carboxyl groups, respectively, were shifted to higher wavenumbers of 1616.0 and 1423.4 cm$^{-1}$ after crosslinking, which indicated that the crosslinking reaction happened between carboxyl groups of SA and Zr(IV) ions. After Pb$^{2+}$ adsorption onto Fe$_3$O$_4$@SA–Zr, carboxyl groups obviously shifted to 1598.0 and 1415.7 cm$^{-1}$, respectively, which indicated that carboxyl groups were involved in the adsorption of Pb$^{2+}$ ions and Pb$^{2+}$ ions adsorption onto Fe$_3$O$_4$@SA–Zr was mainly through the formation of Pb$^{2+}$–COO$^-$ complex. The peaks representing –OH groups shifted to 3423.7 and 1033.9 cm$^{-1}$ after Pb$^{2+}$ adsorption, indicating the participation of hydroxyl groups in the adsorption process. In addition, the peak at around 582.3 cm$^{-1}$ corresponding to Fe–O bond was found to shift to 586.0 cm$^{-1}$, which indicated that Fe$_3$O$_4$ was also involved in Pb$^{2+}$ adsorption through the surface hydroxyl groups.

XRD pattern of Fe$_3$O$_4$@SA–Zr was shown in Supplementary Fig. S3b. Six diffraction peaks at 2θ = 30.5°, 35.6°, 43.3°, 53.7°, 57.3° and 62.8° were observed, which were assigned to the characteristic peaks of iron oxide particles (Niu et al., 2012). Therefore, Fe$_3$O$_4$ were successfully embedded in sodium alginate matrix by the crosslinking reaction of carboxyl groups and Zr$^{4+}$ ions. Saturation magnetization value of Fe$_3$O$_4$@SA–Zr was 7.88 emu/g. When a permanent magnet was placed near the bottle wall, the magnetic Fe$_3$O$_4$@SA–Zr was immediately attracted to the wall (Supplementary Fig. S4). These results indicated that magnetic property provided a rapid and efficient way to separate Fe$_3$O$_4$@SA–Zr from the treated solution using an external magnetic field, which was especially important for the practical applications. From the results
of FTIR and VSM, the presence of Fe$_3$O$_4$ in the polymer beads not only was used as a magnetic separation medium, but also had adsorption ability and made a contribution to the adsorption capacity.

3.2. Effect of initial pH

As shown in Fig. 1a, the adsorption of Pb$^{2+}$ ions increased rapidly as solution pH increased from 1 to 2, then increased slowly and obtained the maximum adsorption capacity at pH about 5–6. It was suggested that Pb$^{2+}$ ions were effectively removed at a wide pH range using Fe$_3$O$_4$@SA–Zr as an adsorbent. The adsorption experiments were not conducted at pH higher than 6.0 to avoid the hydrolyzation of Pb$^{2+}$ ions as the insoluble hydroxides. Thus, solution pH of about 5.0 was chosen for further adsorption experiments.

To test the stability of Fe$_3$O$_4$@SA–Zr during the adsorption process, the leakage of Fe and Zr ions was analyzed. It was found that the release of Fe ions from Fe$_3$O$_4$@SA–Zr was mainly occurred under acidic condition and decreased with the increase in solution pH. The dissolved Fe ions were lower than 0.14 mg/L as solution pH was close to neutral pH. However, the leaching of Zr ions was very low within pH range of 1–6. This indicated the perfect stability of Fe$_3$O$_4$@SA–Zr during the adsorption process. The crosslinking reaction between the carboxyl groups of SA and Zr cations was expected to form a three-dimensional crosslinking structure, thus forming a barrier to reduce Fe$_3$O$_4$ aggregation and prevent Fe leaching from the polymer beads during the adsorption process, as a result, Fe$_3$O$_4$@SA–Zr exhibited greater stability in a wide pH range.

3.3. Effect of initial metal concentration and temperature and adsorption isotherms

The effect of initial Pb$^{2+}$ concentration on the adsorption of Pb$^{2+}$ ions onto Fe$_3$O$_4$@SA–Zr was shown in Fig. 1b. It was observed that the adsorption capacity of Pb$^{2+}$ ions increased from 25 to 290 mg/g when the initial Pb$^{2+}$ concentration increased from 50 to 800 mg/L at 303 K, while the removal efficiency of Pb$^{2+}$ ions decreased from 100% to 72.5%. The decrease of removal percentage might be due to the saturation of binding sites at higher metal concentrations. However, when the initial Pb$^{2+}$ concentration was lower than 200 mg/L, almost 100% of Pb$^{2+}$ ions was removed from the solution, indicating that Fe$_3$O$_4$@SA–Zr can be used as an effective adsorbent to treat polluted water with low concentration of Pb$^{2+}$ ions (<200 mg/L). Moreover, the effect of temperature on the adsorption capacity was also examined, and it was observed that the adsorption capacity of Fe$_3$O$_4$@SA–Zr for Pb$^{2+}$ ions increased with the decrease of temperature for each initial Pb$^{2+}$ concentration, indicating that the adsorption process of Pb$^{2+}$ ions on Fe$_3$O$_4$@SA–Zr was exothermic in nature.

Langmuir, Freundlich, Dubinin–Radushkevich (D–R) isotherm models were used to describe the adsorption equilibrium. Langmuir and Freundlich isotherms can be expressed as (Zheng et al., 2012):

$$C_e/Q_e = 1/bQ_{\text{max}} + C_e/Q_{\text{max}}$$

(3)

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$$

(4)
where \( b \) (L/mg) and \( Q_{\text{max}} \) (mg/g) are the Langmuir constant and the maximum adsorption capacity, respectively. \( K_s \) and \( 1/n \) are the Freundlich constants, which are related to the adsorption capacity and adsorption intensity, respectively. The Dubinin–Radushkevich (D–R) isotherm model can be expressed as:

\[
\ln Q_e = \ln Q_m - \beta e^2
\]

where \( Q_e \) (mg/g) is the amount of Pb\(^{2+}\) adsorbed at equilibrium, \( Q_m \) (mg/g) is the maximum adsorption capacity, \( \beta \) (mol\(^2\)/kJ\(^2\)) is a constant related to adsorption energy, \( e \) (kJ/mol) is the polanyi potential, which is equal to:

\[
e = RT \ln \left(1 + \frac{1}{C_0}ight)
\]

where \( R \) (J/mol/K) is the gas constant, \( T \) (K) is the absolute temperature.

The mean free energy, \( E \) (kJ/mol), is calculated by:

\[
E = \frac{1}{\sqrt{2b}}
\]

If the \( E \) value is lower than 8 kJ/mol, the adsorption process belongs to the physical adsorption. If the \( E \) value is higher than 8 kJ/mol, the adsorption process belongs to the chemical adsorption (Zheng et al., 2012).

The Langmuir and Freundlich isotherm constants along with correlation coefficients (\( R^2 \)) were calculated from the corresponding isotherms and the results were listed in Table 1. As shown in Table 1, the \( R^2 \) values obtained from the Langmuir isotherm were all higher than 0.992 and the theoretical \( Q_{\text{max}} \) values were very close to those experimentally obtained, indicating that the adsorption of Pb\(^{2+}\) ions on Fe\(_3\)O\(_4\)@SA–Zr was well described by the Langmuir isotherm. The maximum adsorption capacities of Pb\(^{2+}\) ions onto Fe\(_3\)O\(_4\)@SA–Zr were calculated to be 333.33, 294.12 and 217.39 mg/g at 293, 303 and 313 K, respectively. The Langmuir isotherm fitted the experimental data very well may be due to the homogeneous nature of active sites on the surface of Fe\(_3\)O\(_4\)@SA–Zr, a monolayer adsorption occurred between the polymer beads and Pb\(^{2+}\) ions. Langmuir constant \( b \) relating to the affinity of binding sites decreased as the temperature increased, which indicated that the adsorption intensity became weaker at higher temperatures. The maximum adsorption capacity of Pb\(^{2+}\) ions onto Fe\(_3\)O\(_4\)@SA–Zr polymer beads for Pb\(^{2+}\) ions (333.33 mg/g) was higher than those of other adsorbents in the literatures, such as polyaniline/calcium alginate beads (251.45 mg/g) (Jiang et al., 2012), poly(vinyl alcohol)/chitosan beads (166.44 mg/g) (Li et al., 2011b), alginate/montmorillonite composite beads (244.6 mg/g) (Shawky, 2011), activated carbon with Phmerochea chrysosporium immobilised in calcium alginate beads (136.6 mg/g) (Lai et al., 2008), γ-Fe\(_2\)O\(_3\) functionalizing with citrate ions encapsulated into calcium alginate beads (97.4 mg/g) (Bee et al., 2011), nanohydroxyapatite–alginate composite films (270.3 mg/g) (Googerdchian et al., 2012). In addition, from Table 1, it was also observed that the value of \( E \) for the adsorption of Pb\(^{2+}\) was calculated to be 15.08, 16.78 and 9.28 kJ/mol at 293, 303 and 313 K, respectively, indicating that the adsorption of Pb\(^{2+}\) onto Fe\(_3\)O\(_4\)@SA–Zr was a chemical adsorption process.

### 3.4. Effect of contact time and adsorption kinetics

As shown in Fig. 1c, the amount of Pb\(^{2+}\) ions adsorbed onto Fe\(_3\)O\(_4\)@SA–Zr increased with an increase in contact time and higher removal efficiencies were obtained in a shorter time. High adsorption capacity and rapid adsorption rate suggested the strong affinity of Fe\(_3\)O\(_4\)@SA–Zr towards Pb\(^{2+}\) ions, which may be due to the presence of a large number of the functional groups. Moreover, Fe\(_3\)O\(_4\)@SA–Zr had open pore structure and possessed three-dimensional polymeric network, which would decrease the mass transfer resistance and enhance the diffusion of metal ions into the interior of the polymer beads, resulting in extremely fast adsorption kinetics. It also can be seen that the initial Pb\(^{2+}\) concentration had an obvious effect on the adsorption process to reach the equilibrium. The time needed for the initial Pb\(^{2+}\) concentrations of 50 and 100 mg/L to reach the equilibrium was 90 min, while it took about 150 and 420 min for initial Pb\(^{2+}\) concentration of 200 and 400 mg/L, respectively.

The pseudo-first-order, pseudo-second-order and intraparticle diffusion were applied to investigate the rate-controlling step and mass transfer mechanism involving in the adsorption process of Pb\(^{2+}\) onto Fe\(_3\)O\(_4\)@SA–Zr.

The pseudo-first-order and pseudo-second-order kinetic models are given as:

\[
\ln(Q_e - Q_t) = \ln Q_e - k_1 t
\]

\[
t = \frac{1}{k_2Q_e^2} - \frac{1}{Q_e^2}
\]

where \( Q_e \) and \( Q_t \) (mg/g) are the adsorption capacities at time \( t \) (min) and at equilibrium, respectively. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg/min) are first-order and second-order rate constants, respectively. The initial adsorption rate \( h \) (mg/g/min) can be calculated from \( h = k_2Q_e^2 \).

### Table 1

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>D–R isotherm</th>
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<td>( Q_{\text{max}} ) (mg/g)</td>
<td>( K_s ) (L/mg)</td>
<td>( R^2 )</td>
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<td>303</td>
<td>294.12</td>
<td>0.18</td>
<td>0.9931</td>
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<tr>
<td>313</td>
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### Table 2

Kinetic parameters of pseudo-first order, pseudo-second order and intraparticle diffusion for Pb\(^{2+}\) adsorption onto Fe\(_3\)O\(_4\)@SA–Zr beads.

<table>
<thead>
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</tr>
</thead>
<tbody>
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<td>50 mg/L</td>
</tr>
<tr>
<td>Pseudo-first order ( Q_e ) (mg/g)</td>
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<tr>
<td>( k_1 \times 10^{-2} ) (1/min)</td>
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<tr>
<td>( R^2 )</td>
</tr>
<tr>
<td>Pseudo-second order ( Q_e ) (mg/g)</td>
</tr>
<tr>
<td>( k_2 \times 10^{-5} ) (g/(mg min))</td>
</tr>
<tr>
<td>( h ) (mg/(g min))</td>
</tr>
<tr>
<td>( R^2 )</td>
</tr>
<tr>
<td>Intraparticle diffusion ( K_{\text{diff}} ) (mg/(g min(^{1/2})))</td>
</tr>
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<td>( C_1 )</td>
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<tr>
<td>( R^2 )</td>
</tr>
<tr>
<td>( K_{\text{diff}} ) (mg/(g min(^{1/2})))</td>
</tr>
<tr>
<td>( R^2 )</td>
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</table>
As shown in Table 2, the pseudo-first-order kinetic model was insufficient to describe the adsorption process of Pb\(^{2+}\) ions with low correlation coefficients. Whereas the plots of ln \(Q_t\) versus \(t\) showed good linearity at different initial Pb\(^{2+}\) concentrations and the calculated correlation coefficients \((R^2)\) were all higher than 0.999. The theoretical \(Q_t\) values were very close to the experimental values. These results indicated that the adsorption of Pb\(^{2+}\) onto Fe\(_2\)O\(_4\)@SA–Zr followed the second-order rate model and chemical reaction occurred between Pb\(^{2+}\) ions and functional groups on the surface of Fe\(_2\)O\(_4\)@SA–Zr. Fe\(_2\)O\(_4\)@SA–Zr was a composite material, alginic can provide abundant carboxyl groups and hydroxyl groups while Fe\(_2\)O\(_4\) can provide surface hydroxyl groups, which can be used as active sites for Pb\(^{2+}\) ion exchange and chelation. In addition, the obtained initial adsorption rates, \(h\), were found to increase with an increase of the initial metal concentration from 50 to 100 mg/L and then decreased, indicating a more rapid adsorption of Pb\(^{2+}\) onto Fe\(_2\)O\(_4\)@SA–Zr at a lower initial metal concentration.

Intraparticle diffusion model was used to describe the diffusion mechanism of Pb\(^{2+}\) ions into the interior of Fe\(_2\)O\(_4\)@SA–Zr, which can be expressed by:

\[
Q_t = K_{id}t^{0.5} + C
\]

(10)

where \(Q_t\) (mg/g) is the amount of Pb\(^{2+}\) adsorbed at time \(t\) (min), \(K_{id}\) (mg/g/min\(^{0.5}\)) is the rate constant of intraparticle diffusion, the intercept \(C\) represents the thickness of boundary layer.

However, the plots of \(Q_t\) versus \(t^{0.5}\) at different initial Pb\(^{2+}\) concentrations showed the multi-linearity over the whole time range, indicating that intraparticle diffusion was not the only rate-limiting mechanism. Adsorption kinetics of Pb\(^{2+}\) ions was controlled by different mechanisms, involving the rapid surface adsorption, intraparticle diffusion and the final equilibrium. At the initial stage, a large number of vacant active sites were available for Pb\(^{2+}\) ions, adsorption was mainly the rapid external diffusion and reactive adsorption between Pb\(^{2+}\) ions and functional groups on the surface of polymer beads. Whereas with the gradual occupancy of these binding sites, a concentration gradient would be formed between the surface and interior of the polymer beads, which promoted the diffusion of the Pb\(^{2+}\) ions into the interior of the beads, and the adsorption rate became dependent on the rate associated with intraparticle diffusion. The \(K_{id}\) and \(C\) values were calculated and listed in Table 2. It was observed that the value of \(K_{id}\) increased from 1.47 to 10.71 mg/g/min\(^{0.5}\) when the initial Pb\(^{2+}\) concentration increased from 50 to 400 mg/L. Higher values of \(C\) indicated that surface adsorption played an important role in the adsorption of Pb\(^{2+}\) ions. From the obtained results, the adsorption process of Pb\(^{2+}\) ions onto Fe\(_2\)O\(_4\)@SA–Zr beads was mainly controlled by interacting with the surface binding sites and diffusion into the interior of the polymer beads.

3.5. Adsorption thermodynamics

To analyze the thermodynamic behaviors of the adsorption of Pb\(^{2+}\) ions onto Fe\(_2\)O\(_4\)@SA–Zr, the thermodynamic parameters including the Gibbs free energy \((\Delta G^\circ)\), enthalpy change \((\Delta H^\circ)\) and entropy change \((\Delta S^\circ)\) are calculated by the following equations:

\[
\Delta G^\circ = -RT \ln K_d
\]

(11)

\[
\ln K_d = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}
\]

(12)

where \(R\) is the universal gas constant (8.314 J/mol/K) and \(K_d\) is the equilibrium constant \((Q_e/C_e)\). The values of \(\Delta H^\circ\) and \(\Delta S^\circ\) can be calculated from the slope and intercept of the linear plot of \(\ln K_d\) versus \(1/T\), respectively. It was found that the negative values of \(\Delta G^\circ\) increased from −6.62 to −1.49 kJ/mol when the temperature increased from 293 to 313 K, indicating that the adsorption of Pb\(^{2+}\) ions onto Fe\(_2\)O\(_4\)@SA–Zr was more favorable at low temperatures and the adsorption process was spontaneous and feasible under the experimental conditions. The negative value of \(\Delta H^\circ\) suggested that the adsorption of Pb\(^{2+}\) ions was exothermic in nature. The negative of \(\Delta S^\circ\) indicated that the randomness was decreased at the solid/liquid interface during the adsorption process.

3.6. Effect of ionic strength and HA

The presence of salts in wastewater results in a high ionic strength, which may affect the adsorption behaviors of Fe\(_2\)O\(_4\)@SA–Zr for Pb\(^{2+}\) ions. The effect of ionic strength on the adsorption performance of Fe\(_2\)O\(_4\)@SA–Zr was studied and the results were presented in Fig. 1d. It can be seen that the presence of Na-electrolyte did not significantly decrease the adsorption of Pb\(^{2+}\) ions (8.51%) on Fe\(_2\)O\(_4\)@SA–Zr. However, a decrease of about 45.65% in Pb\(^{2+}\) adsorption was observed when the concentration of CaCl\(_2\) reached up to 0.1 mol/L. Ca\(^{2+}\) ions with a higher valency than Na\(^+\) ions exhibited a stronger competition with Pb\(^{2+}\) ions for the available active sites and thus hindered the Pb\(^{2+}\) adsorption. This was consistent with some studies that Ca-electrolyte had significant negative impact on adsorption of Pb and Cd ions by tripolyphosphate-impregnated Kaolinite clay (Unuabonah et al., 2007) and adsorption of Pb and Cu ions by waste beer yeast (Han et al., 2006). Natural organic matter is widely present in natural aquatic environments, which can be adsorbed on the adsorbent and change the surface properties of adsorbent. Therefore, the effect of natural organic matter such as humic acid (HA) on the adsorption behaviors of Fe\(_2\)O\(_4\)@SA–Zr for Pb\(^{2+}\) ions was conducted and the obtained results were shown in Fig. 1d. It was found that increasing of HA concentration from 2 to 20 mg/L almost had no effect on the adsorption of Pb\(^{2+}\) ions. The similar phenomenon was reported in the adsorption of Cu(II), Pb(II), and Cd(II) onto Fe\(_2\)O\(_4\)@SiO\(_2\) (Wang et al., 2010). This indicated that the affinity of Fe\(_2\)O\(_4\)@SA–Zr towards Pb\(^{2+}\) ions was much higher than that of HA. Fe\(_2\)O\(_4\)@SA–Zr could be efficiently used for the removal of Pb\(^{2+}\) ions from aqueous solutions containing natural organic matter, like HA.

3.7. Competitive adsorption

The competitive absorption experiments were conducted in the binary-metal system to examine the selectivity of Fe\(_2\)O\(_4\)@SA–Zr. The initial concentration of each metal ion in the mixture was 100 mg/L. The distribution coefficient \((K_d)\) and selectivity coefficient \((K_s)\) can be obtained by Eqs. (13) and (14):

\[
K_d = \frac{Q_e}{C_e}
\]

(13)

\[
K_s = \frac{K_d(\text{Pb}^{2+})}{K_d(\text{M}^{2+})}
\]

(14)

where \(K_d\) is the distribution coefficient, \(K_s\) is the selectivity coefficient, and \(\text{M}^{2+}\) represents Cu\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\) and Zn\(^{2+}\) ions.

The calculated \(K_d\) and \(K_s\) values were listed in Table 3. In the binary-metal system, the adsorption of Pb\(^{2+}\) ions was not affected.
in the presence of competing cations such as Cu\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\) and Zn\(^{2+}\). When the four metals were present, the removal percentage of Pb\(^{2+}\) was over 99%. The K_d value of Fe\(_3\)O\(_4\)@SA–Zr for Pb\(^{2+}\) was far greater than that for Cu\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\) and Zn\(^{2+}\). The higher K_d values of Fe\(_3\)O\(_4\)@SA–Zr for Pb\(^{2+}\)/Cu\(^{2+}\), Pb\(^{2+}\)/Cd\(^{2+}\), Pb\(^{2+}\)/Hg\(^{2+}\) and Pb\(^{2+}\)/Zn\(^{2+}\) suggested that the binding ability of Fe\(_3\)O\(_4\)@SA–Zr for Pb\(^{2+}\) was significantly stronger than that for Cu\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\) and Zn\(^{2+}\). The above results indicated that Fe\(_3\)O\(_4\)@SA–Zr had high selectivity for the separation/recovery of Pb\(^{2+}\) from Pb\(^{2+}\)/Cu\(^{2+}\), Pb\(^{2+}\)/Cd\(^{2+}\), Pb\(^{2+}\)/Hg\(^{2+}\) and Pb\(^{2+}\)/Zn\(^{2+}\) mixture.

3.8. Adsorption mechanism

To deeply investigate the mechanism governing the removal process of Pb\(^{2+}\) ions onto Fe\(_3\)O\(_4\)@SA–Zr, the XPS analysis of virgin and Pb\(^{2+}\)-loaded Fe\(_3\)O\(_4\)@SA–Zr polymer beads was performed. The XPS wide scans of Fe\(_3\)O\(_4\)@SA–Zr before and after Pb\(^{2+}\) adsorption were shown in Supplementary Fig. S5a. From Supplementary Fig. S5a, the major peaks such as C 1s, O 1s, Fe 2p and Zr 3d were present. A new peak assigning to Pb 4f was clearly observed for Pb\(^{2+}\)-loaded adsorbent, confirming the adsorption of Pb\(^{2+}\) onto Fe\(_3\)O\(_4\)@SA–Zr. The O 1s spectrum of Fe\(_3\)O\(_4\)@SA–Zr (Supplementary Fig. S5b) showed four peaks at 532.30, 531.47, 530.50 and 529.00 eV, respectively, which could be assigned to the O atom in COO\(^-\), C–O, hydroxyl bonded to metal (M–OH) (M:Fe or Zr) and metal oxide (M–O), respectively (Zheng et al., 2012; Ren et al., 2012). After Pb\(^{2+}\) adsorption, the O 1s spectrum changed. The area ratio for the peaks at 532.30 eV and 530.50 eV decreased from 12.08% to 18.31%. The high resolution scan of Fe 2p for the peaks at 532.30 eV and 530.50 eV decreased from 26.17% to 708.39 and 710.01 eV, respectively. These results indicated that Pb\(^{2+}\) ions were involved in Pb\(^{2+}\) adsorption through the formation of carboxyl-metal and M–O–metal complexes, which were consistent with the FTIR analysis. The high resolution Zr 3d spectrum of Fe\(_3\)O\(_4\)@SA–Zr produced two peaks at 181.83 and 184.26 eV. After Pb\(^{2+}\) adsorption, the binding energies shifted to 181.61 and 183.99 eV, respectively. The adsorption experiments were carried out at pH close to neutral, the leakage of Fe and Zr was very low, which indicated that ion exchange between Pb\(^{2+}\) ions and Fe and Zr was negligible. Since Zr\(^{4+}\) ions are easily hydrolyzed in aqueous solutions and form tetranuclear or octanuclear species, which are further deprotonated by releasing hydrogen ions to form hydroxyl ions and water molecules on its surface (Balaji et al., 2005; Biswas et al., 2008), these active hydroxyl ions can take part in the ligand exchange with the metal ions, in which O atoms donated electrons to Pb\(^{2+}\) ions and the electron cloud density at the adjacent Zr atoms was decreased. Supplementary Fig. S5e showed the Pb 4f spectrum of Pb\(^{2+}\)-loaded adsorbent, and the peaks at 142.72 eV and 137.86 eV could be ascribed to Pb 4f 5/2 and Pb 4f 7/2, respectively. The binding energies of Pb 4f 5/2 and Pb 4f 7/2 in Pb(NO\(_3\))\(_2\) were centered at 145.0 and 139.9 eV, respectively (Pan et al., 2010), and a significant shift to low binding energies was observed after Pb\(^{2+}\) adsorption onto Fe\(_3\)O\(_4\)@SA–Zr, suggesting that specific reaction occurred between Pb\(^{2+}\) and Fe\(_3\)O\(_4\)@SA–Zr.

3.9. Column studies

Continuous flow operation in fixed-bed column mode is an effective and economically feasible process for the removal of heavy metal ions from aqueous solution because it makes the most efficient use of the adsorption capacity and results in a high degree of purification of the effluent. High adsorption capacity, rapid kinetics and spherical structure made Fe\(_3\)O\(_4\)@SA–Zr applicable to the continuous column operations. Thus, the suitability of Fe\(_3\)O\(_4\)@SA–Zr in the fixed-bed column operation was investigated and breakthrough curves were obtained at different flow rates and influent metal concentrations. The total adsorption capacity (Q_\text{exp} mg/g) and removal percentage of the column for Pb\(^{2+}\) ions were calculated by evaluating the breakthrough curves at different flow rates and different influent Pb\(^{2+}\) concentration.

Breakthrough curves at flow rates of 2.0 and 4.0 mL/min were obtained at bed height of 7.5 cm and influent Pb\(^{2+}\) concentration of 50 mg/L. As shown in Fig. 2a, an increase in flow rate, breakthrough time decreased significantly. The fixed-bed column filling with 2.0 g of Fe\(_3\)O\(_4\)@SA–Zr could purify 8880 and 6000 mL of Pb\(^{2+}\) solutions with the influent Pb\(^{2+}\) concentration of 50 mg/L at flow rates of 2.0 and 4.0 mL/min, respectively, then the concentration of Pb\(^{2+}\) ions in the effluent increased with the passed volume till the adsorption column reached saturation at 32520 and 37440 mL of Pb\(^{2+}\) solutions, respectively. Flow rate greatly affected the total adsorption capacity and removal efficiency of the fixed-bed column. This can be explained by the fact that the residence time of Pb\(^{2+}\) ions in the column at lower flow rate was longer than that at higher flow rate, Pb\(^{2+}\) ions had more time to interact with active sites on the surface of the adsorbent and further diffuse within the pores, resulting in higher removal efficiency of Pb\(^{2+}\) ions in fixed-bed column.

Breakthrough curves at influent Pb\(^{2+}\) concentrations of 50, 100 and 200 mg/L were obtained at a fixed bed height of 7.5 cm and flow rate of 2.0 mL/min (Fig. 2b). At influent metal concentrations of 50 and 100 mg/L, the breakthrough curves followed the typical

![Fig. 2. Breakthrough curves for Pb\(^{2+}\) adsorption onto Fe\(_3\)O\(_4\)@SA–Zr at different flow rates (a) and different influent metal concentration (b).](image-url)
S-shaped curves, however, a near linear increase in influent metal concentration of 200 mg/L was found. It was observed that increasing the influent metal concentration from 50 to 200 mg/L, breakthrough time, exhaustion time and the treated volume shifted markedly to the left, as a result, the breakthrough curve became steeper and the service time of the bed decreased significantly. Only a given layer of bed height in the column could be in contact with Pb\(^{2+}\) ions, so the higher influent metal concentration, the less available active sites to bind with Pb\(^{2+}\) ions. As a result, the binding sites saturated quickly and left more Pb\(^{2+}\) ions unadsorbed in the solution, which resulted in earlier breakthrough and exhaustion time as well as the reduction of the treated volume at higher influent Pb\(^{2+}\) concentration.

Thomas model is widely used to describe the column adsorption data and calculate the kinetic constants and the maximum adsorption capacity. Thomas model is expressed by Eq. (15) (Malkoc and Nuhoglu, 2006):

\[
\frac{C_t}{C_0} = 1 + \exp\left(\frac{k_{th} Q}{q_{th}} m - C_o V_e\right)
\]

where \(V_e\) is the effluent volume (L), \(k_{th}\) is the rate constant (mL/mg/min) and \(q_{th}\) is the maximum adsorption capacity (mg/g).

The total amount of Pb\(^{2+}\) adsorbed and removal efficiency at different operating parameters as well as the Thomas model parameters were presented in Table 4. As can be seen in Table 4, total amount of Pb\(^{2+}\) adsorbed and removal efficiency were highest at influent Pb\(^{2+}\) concentration of 50 mg/L and flow rate of 2.0 mL/min. Maximum removal efficiency of Fe\(_3\)O\(_4@SA–Zr\) for Pb\(^{2+}\) ions decreased with increasing flow rate and influent Pb\(^{2+}\) concentration, the similar results have been found for uranium adsorption onto Ca–alginate immobilised Trichoderma harzianum (Akhtar et al., 2009) and Reactive black 5 adsorption onto polysulfone-immobilised Corynebacterium glutamicum (Vijayaraghavan and Yun, 2008).

The Thomas model with higher correlation coefficients \((R^2 > 0.96)\) for Pb\(^{2+}\) adsorption indicated the validity of the Thomas model for the present fixed-bed columns. The Thomas maximum adsorption capacities \((q_{th},\text{mg/g})\) were in good agreement with the experimental \(Q_{exp}\) values. The Thomas rate constant \((k_{th},\text{mL/mg/min})\) represents the rate of metal ions transfer from the solution to the surface of the solid. As seen in Table 4, the \(q_{th}\) values decreased and \(k_{th}\) values increased with increasing the flow rate. The data in Table 4 also showed that the \(q_{th}\) values decreased with increasing influent Pb\(^{2+}\) concentration, while the \(k_{th}\) values first increased and then decreased with the increase of influent Pb\(^{2+}\) concentration, which may be due to the fact that a competition occurred between Pb\(^{2+}\) ions for the available active sites at higher influent Pb\(^{2+}\) concentration, resulting in more unadsorbed Pb\(^{2+}\) ions leaving the adsorption column. As a result, the adsorption rate of Fe\(_3\)O\(_4@SA–Zr\) for Pb\(^{2+}\) ions decreased.

### 3.9.1. Reusability studies

The reusability of Fe\(_3\)O\(_4@SA–Zr\) is an important aspect to evaluate its potential for practical application because the reusability can obviously reduce the operation cost and make the process economical. Desorption of Pb\(^{2+}\) from the metal-loaded polymer beads was carried out in a batch mode by using 0.1 mol/L HCl solution as eluent and the desorption efficiency was up to 97.77%. It was found that the adsorption capacity of Fe\(_3\)O\(_4@SA–Zr\) for Pb\(^{2+}\) ions was only decreased by about 8% after 10 successive adsorption–desorption cycles. There is no significant damage was observed and the spherical shape of Fe\(_3\)O\(_4@SA–Zr\) polymer beads was well maintained. Magnetic response of Fe\(_3\)O\(_4@SA–Zr\) after 10 adsorption–desorption cycles was also studied. It was found that the Fe\(_3\)O\(_4@SA–Zr\) quickly gathered on the bottle wall 5 cm far from the external magnet (Supplementary Fig. S6). It was suggested that Fe\(_3\)O\(_4@SA–Zr\) still retained higher magnetism and could be separated quickly and efficiently from aqueous solutions even after 10 adsorption–desorption operations. These results indicated that Fe\(_3\)O\(_4@SA–Zr\) with high stability could be effectively and economically used for the treatment of wastewater containing Pb\(^{2+}\) ions.

### 4. Conclusions

Magnetic macroporous Fe\(_3\)O\(_4@SA–Zr\) was prepared and characterized. Fe\(_3\)O\(_4@SA–Zr\) had higher adsorption capacity and effectively removed Pb\(^{2+}\) in a wide pH range. The adsorption of Pb\(^{2+}\) onto Fe\(_3\)O\(_4@SA–Zr\) followed Langmuir isotherm and pseudo-second-order kinetics and the adsorption process was spontaneous and exothermic in nature. Column results showed that decreasing of flow rate and influent Pb\(^{2+}\) concentration resulted in highly efficient removal of Pb\(^{2+}\) from aqueous solutions due to high efficiency, fast kinetics and good reusability, as well as low-cost, simple preparation and convenient separation.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [http://dx.doi.org/10.1016/j.biortech.2013.05.081](http://dx.doi.org/10.1016/j.biortech.2013.05.081).


