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Synthesis and characterization of whisker surface imprinted polymer and selective solid-phase extraction of trace Sr(II) from environment aqueous solution

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ABSTRACT

A novel surface ion-imprinted polymer (S-IIP) has been synthesized by surface ion-imprinting concept in the presence of sodium trititanate whisker, Sr(II), chitosan and γ-glycidoxypropyl trimethoxysilane (KH-560) for selective solid-phase extraction of trace Sr(II) from environment aqueous solution. Characterizations of S-IIP were achieved by infrared spectra and surface area measurement. S-IIP was used in the sorption–desorption process; the effect of solution pH, sorbent amount, and flow rate on the extraction of Sr(II) ions from aqueous solutions was investigated. The adsorption kinetics and isotherm were also obtained in detail. The dynamical study showed it was well followed the pseudo-second-order kinetic equation in the adsorption process. Meanwhile, the equilibrium adsorption studies showed that it very good fit the Langmuir isotherm equation for the monolayer adsorption process, and the maximum adsorption capacity was 32.60 mg/g. Selectivity experiments showed that S-IIP had a higher selectivity than non-imprinted polymer. The thermodynamic parameters (positive values ΔG°, ΔH°, and ΔS°) confirmed the non-spontaneous, endothermic, and entropy gained nature within the temperature range evaluated. The precision relative standard deviation and detection limit of this method were 0.93% and 0.30 μg/L, respectively, and it was successfully applied to the determination of trace Sr(II) in different wastewater samples with satisfactory results using inductively coupled plasma atomic emission spectrometry.

Keywords: Solid-phase extraction; Sr(II); Selective recognition; Isotherms; Kinetics; Thermodynamics

1. Introduction

Strontium is present in the earth's crust at an average concentration of 0.04% and is therefore 15th in abundance [1]. Unfortunately, Sr(II) is the concerned contaminant due to its high yield in spent nuclear fuel and long half-life of 27.7 years. Sr(II) can get into the food chain through the soil, water directly or indirectly and was accumulated in the bones, muscles, not readily available in the course of human body metabolism, seriously endangering human health [2,3]. So, removal of trace strontium nuclide from aqueous solutions is more and more significant. At present, a lot of ways can achieve the separation/enrichment including: co-precipitation, ion-exchange resins, organic-solvent extraction, separation, and enrichment

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by chitosan (CTS) [4–8]. But these methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems. It is widely confirmed that ion-imprinted polymer (IIP) adsorbents are tailor-made materials with high selectivity for a target ion [9–11]. IIP can be synthesized in three different imprinting approaches as follows: the non-covalent, the covalent, and the semi-covalent. In all these protocols, a template interacts with an appropriate functional monomer to establish specific interactions. However, IIP synthesized by traditional methods exhibits high affinity and selectivity but poor site accessibility to the target analytes due to the highly embedment. Thus, several studies have reported IIP based on surface imprinting and IIP prepared by this method shows a lot of advantages such as high adsorption selectivity, more accessible sites, and fast binding kinetics [12–16]. Currently, a particularly promising application of surface ion-imprinted polymer (S-IIP) is the selective solid-phase extraction (SPE) pre-separation/enrichment of analytes present in low concentration in a complex matrix. SPE is one of the widely used and fast emerging pre-concentrative/separation techniques due to the following advantages [17,18]: (1) absence of emulsion; (2) high enrichment factor; (3) flexibility; (4) safety and easy of automation; (5) economical and environmental-friendly; (6) speed and simplicity. For example, Rao et al. [19] have reviewed various IIP-SPE procedures developed for enrichment-separation of inorganic materials.

The aim of this study was to synthesize a S-IIP using CTS as the functional monomer [20,21], Sr(II) ions as template, KH-560 as cross-linker, and sodium trititanate whisker as matrix. The S-IIP was without any environmental problems and used for selective SPE and determination of Sr(II) in environment aqueous solutions. The experimental parameters that affect the adsorption capacity including pH, adsorbent amount, and flow rate were evaluated and optimized. The adsorption kinetics and isotherms and thermodynamics of S-IIP were also described in detail. The method was successfully applied to the determination of trace Sr(II) in different wastewater samples with satisfactory results.

2. Experimental

2.1. Apparatus

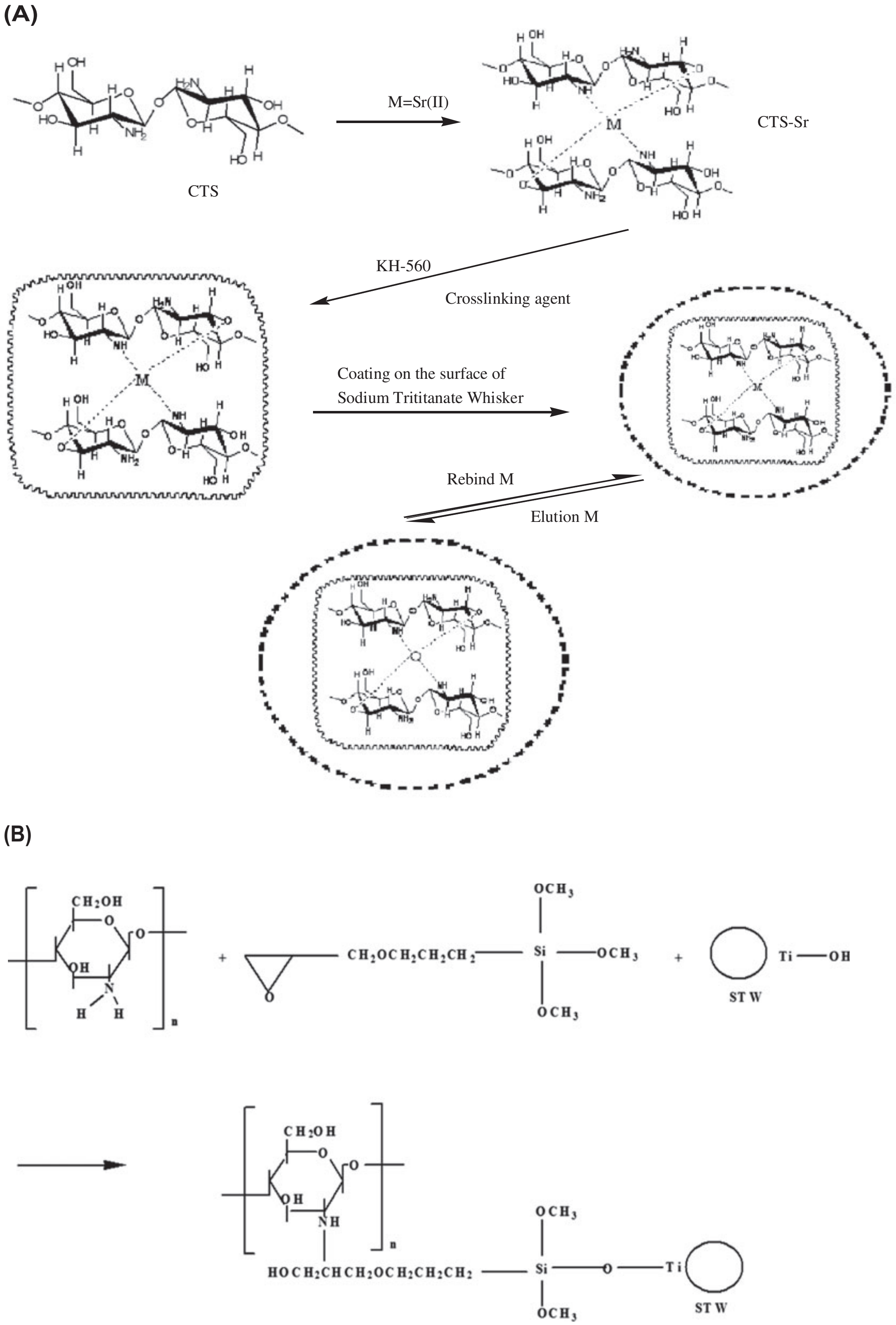
Vista-MPX inductively coupled plasma atomic emission spectrometry (ICP-AES) (Wollian, USA) was used to determine the concentration of metal ions. And analytical wavelength of determined elements by ICP-AES was Co 238.892 nm, Ni 231.604 nm, Cs 697.327 nm, Ce 418.659 nm, Pb 220.353 nm, Sr 407.771 nm, Zn 213.857 nm, Na 588.995 nm, and Ca 393.366 nm. A pHS-3C digital pH meter (Shanghai, Shanghai, China) was used for pH measurements. 802 centrifugal precipitators (Shanghai, Shanghai, China), DHG-9140A Electric thermostat blast oven (Shanghai, Shanghai, China), and SHZ-D(III) circulating water pumps (Beijing, Beijing, China) were used. FT-IR (4,000–400 cm^{-1}) analyses were carried out on Nicolet Avatar 205 FT-IR spectrometer. Scanning electron microscopy images were obtained at 15.0 kV on the field emission scanning electron microscope (SIRION, USA) after gold plating.

2.2. Reagents

CTS with 98% deacetylation and an average molecular weight of 6×10^4 g mol^{-1} (Yuhuan Biomedical Corporation, Shanghai, China) and cross-linking agents (KH-560) (Wuhan University Chemical Factory, Wuhan, China) were used in my work. Sodium trititanate whisker (Shanghai Whisker Composite Material Limited, Shanghai, China) was activated with 3.0 M HNO_3. Sr(II) was used in the $SrCl_2.6H_2O$ form. All the other chemicals used were in analytical grade. Doubly deionized water (DDW) was used throughout this work. Standard stock solution of Sr(II) (1.0 g/L) was prepared by dissolving the required amounts of the metals in a small volume of concentrated nitric acid. Stock solution was diluted to 1 L with DDW, and more dilute standards were prepared daily by dilution of these solution.

2.3. Preparation of S-IIP

The synthetic route of S-IIP based on sodium trititanate whisker is shown in Fig. 1(A), and the reaction of KH-560 with CTS and sodium trititanate whisker is shown in Fig. 1(B). The synthetic route is as follows: 0.2 g of $SrCl_2.6H_2O$ and 2 g of CTS were added to 75 mL 0.1 mol L^{-1} acetic acid aqueous solution. After stirring for 1 h, 12 mL of KH-560 was added to the transparent solution. The mixture was stirred for 4 h and then bathed in an ultrasonic bath for 20 min at power 100 W before 12 g of activated sodium trititanate whisker was added as powder. After stirring for 1 h, the moist mixture was allowed to evaporate at room temperature and ambient pressure for 24 h to complete the reaction. Then, the dry product was grinded thoroughly fine and washed with DDW to remove non-bound Sr(II). The consequent polymer was filtered and treated with 1.0 M HNO_3 for 12 h at 25℃ to completely leach the coordinated Sr(II). The acid-treated



Reaction of KH-560 with CTS and Sodium trititanate whisker

Fig. 1. The synthetic routes of S-IIP(A) and the reaction of KH-560 with CTS and sodium trititanate whisker(B).

sorbent was rinsed several times with DDW, 1.0 M NaOH to ensure complete H^+ neutralization, and the resulting sorbent with Sr(II) cativities was filtered, washed with DDW, and dried under 50℃ vacuum. Then, the product was grounded in a mechanical mortar and then sized by an 200-mesh sieve and stored for further use. The non-imprinted polymer (NIP) was prepared as a blank in parallel without the addition of Sr(II).

2.4. Batch experiments

The S-IIP (0.4 g) was equilibrated with 50 mL of Sr (II) ion solution (10 mg/L), at 25℃ for 2.5 h in a series of 50-mL Stoppered conical flask. The amount of Sr(II) ion in the solution after and before treatment with S-IIP was determined by ICP-AES. The adsorption capacity Q (mg/g), distribution coefficient (K_d) of Sr(II) with respect to Zn(II), Co(II), Ni(II), Ba(II), Cs(I), Ce (III) and Pb(II), selectivity coefficient (K), and relative selectivity coefficient (K') were calculated as the following equations:

$$Q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$K_d = \frac{(C_0 - C_e)V}{mC_e} \quad (2)$$

$$K = \frac{K_d(\mathrm{Sr(II)})}{K_d(M)} \quad (3)$$

$$K = \frac{K_{\mathrm{imprinted}}}{K_{\mathrm{non-imprinted}}} \quad (4)$$

where C_0 and C_e represent initial concentration of metal ions and the concentration after adsorption, respectively, V is the volume of solution, and m is the weight of S-IIP. $K_{d(\mathrm{Sr(II)})}$ is the distribution coefficient of the template metal ion Sr(II) and $K_{d(\mathrm{M})}$ is the distribution coefficient of the competing metal ions. $K_{\mathrm{imprinted}}$ and $K_{\mathrm{non\text{-}imprinted}}$ are the selectivity coefficients of the S-IIP, and NIP, respectively. K' represents the difference of metal adsorption affinity recognition of sites to the imprinted Sr(II) ions between them; the larger the K', the better the imprinted effect showed.

2.5. Desorption and reusability experiments

After having adsorbed metal ion of Sr(II), the S-IIP was treated with three different concentrations of acid solutions at 50℃ water bath. And Sr(II) ions concentrations in the solution were determined at different desorption times by ICP-AES. The desorption ratio (D %) could be calculated from the following expression:

$$\text{Desorption ratio} = \left(\frac{\text{amount of ions desorbed to the elution medium}}{\text{amount of ions adsorbed onto the sorbent}}\right) \times 100\% \quad (5)$$

After each cycle of adsorption–desorption process, the reusability could be determined.

2.6. Column experiments

About 0.4 g of S-IIP was slurred with DDW and then poured in to a glass column (i.d. 5.0 mm) plucked with small portion of glass wool. The column was preconditioned by passing DDW, and then, a solution containing 500 μg of Sr(II) in a volume of 50 mL was passed through the column at a flow rate of 1.5 mL/min after adjusting pH 7.0.

3. Results and discussion

3.1. Characterization

The FT-IR spectra of sodium trititanate whisker, CTS and KH-560, Non-IP, and S-IIP are given in Fig. 2, respectively. A strong and overlapped band around 3,343–3,487 cm^{-1}, from stretching vibration of N–H and O–H in CTS (Fig. 2(b)), obviously became narrow in S-IIP. Compared with CTS, the absorption band of C–OH decreased from 1,090 to 1,075 cm^{-1} in S-IIP, and the characteristic bands of δsN–H at 1,655 cm^{-1} and νasC–N at 1,377 cm^{-1} increased to 1,710 and 1,420 cm^{-1}. All the facts indicated that in the process of mixing CTS and Sr(II) ions, Sr(II) ions interacted with –OH and $-NH_2$ in CTS resulting in CTS array around the Sr(II) ions with a specific geometry. Compared with KH-560 (Fig. 2(c)), the band intensity of $-CH_3$ (at 2,840 cm^{-1}) and $-CH_2-$ (at 2,945 cm^{-1}) significantly decreased and the characteristic feature of epoxy group (at 760 cm^{-1}) vanished in S-IIP. The results confirmed that KH-560 successfully linked with Sr(II)–CTS accompany with ring-opening process. Compared with S-IIP, the intensity of absorption bands for O–H and N–H stretching vibration (around 3,400 cm^{-1}) in NIP was much lower indicating a large number of $-NH_2$ and –OH participated the cross-linking and polymeric reaction.

The surface area (BET method) is as follows: 18.6 m^2/g for S-IIP, 13.2 m^2/g for NIP and 12.8 m^2/g for sodium trititanate whisker. The results obtained

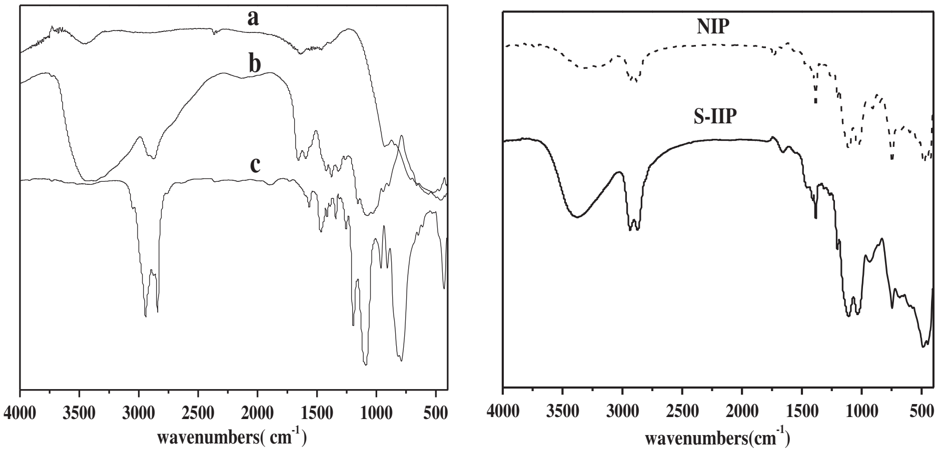


Fig. 2. FT-IR spectrograms of sodium trititanate whisker (a), CTS (b), KH-560 (c) and NIP, S-IIP (on the right).

demonstrate that the surface area of S-IIP is larger than NIP and sodium trititanate whisker.

3.2 Effect of pH

The effects of varying pH on the adsorption of S-IIP and NIP for Sr(II) were investigated using the batch procedures. The adsorption experiments were triplicated, and the results are shown in Fig. 3. In general, the adsorption efficiency of Sr(II) onto S-IIP increased as the pH increased, from a low value of 73% at pH 2.0 to its maximum of 93.75% at pH 7.0. At low pH, the concentration of hydrogen ions caused such amino group protonation that the sorption efficiency of Sr(II) was low. At pH > 6.0, concentration of amino group increased and Sr(II) ions in the solution formed as Sr-NH_3 complex, and as a result, the sorption efficiency increased to 90%. So, pH 7.0 was chosen as optimum for further experiments. Comparing with the S-IIP on the adsorption of Sr(II), NIP had a much lower adsorption efficiency. As in the polymerization and elution process, none of cativities had been formed.

3.3. Effect of sorbent amount

The effect of S-IIP amount on the adsorption of Sr (II) was tested utilizing the batch procedures under pH 7.0 and 25℃ conditions. The results are shown in

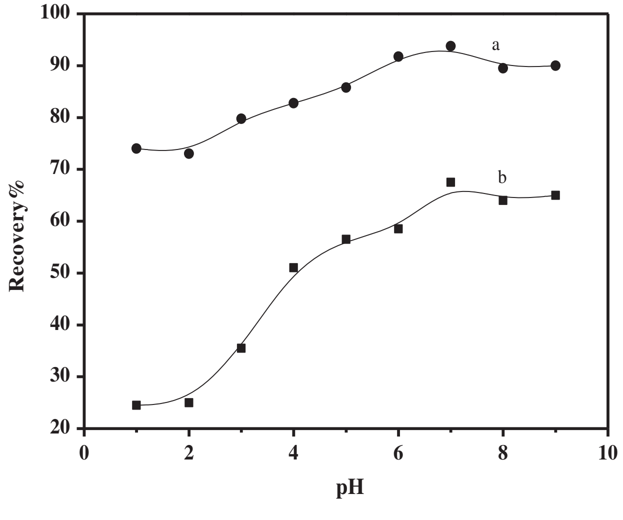


Fig. 3. Effect of pH on the remove of 10 mg/L Sr(II) onto 0.4 g of S-IIP (a) and NIP (b) sorbent for 2.5 h, at 25℃, three parallel determinations.

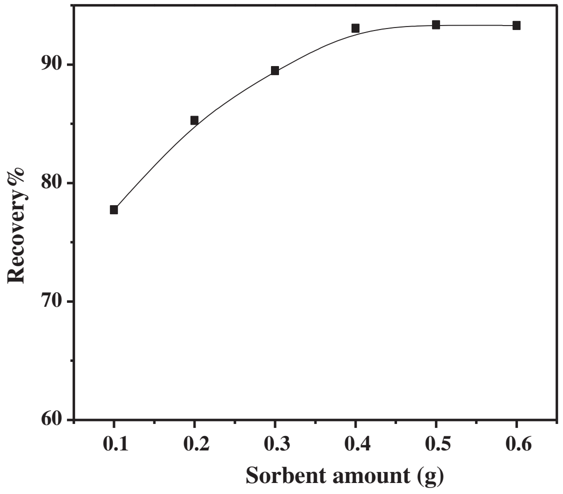


Fig. 4. Effect of S-IIP amount on the remove of 10 mg/L Sr (II) at pH 7.0 for 2.5 h, at 25℃, three parallel determinations.

Fig. 4. It indicated that the adsorption efficiency of Sr(II) onto S-IIP increased as the sorbent amount increased. When the sorbent amount added was 0.4 g, the equilibrium was achieved and the adsorption efficiency was 93.05%. So, 0.4 g of sorbent was chosen for further experiments.

3.4. *Influence of flow rate*

The flow rate of Sr(II) solution through the packed bed column is an important parameter for the time controls of adsorption and analysis using the column procedures, the effect of flow rate on adsorption of Sr(II) was investigated. The results showed that above 2.0 mL/min, the adsorption efficiency was less than 93%. This decrease in adsorption efficiency of Sr(II) ions with increasing flow rate seems due to decreased contact time of Sr(II) with the adsorbent. So, the flow rate of 1.5 mL/min was chosen as optimum for column procedures.

3.5. *Adsorption kinetics*

The adsorption kinetics on the adsorption of Sr(II) onto S-IIP was investigated using 0.4 g S-IIP to equilibrate with 150 mg/L Sr(II) ion solution at 25℃ using the batch procedures. Fig. 5 showed the kinetics of the adsorption of Sr(II) onto S-IIP. It is evident from Fig. 5 that the adsorption was initially rapid and reached equilibrium after approximately 2.5 h. In order to evaluate the kinetic mechanism that controls the adsorption process, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models shown as Eqs. (6)–(9) were employed to interpret the experimental data [22–24]. A good correlation of the kinetic data explains the adsorption mechanism of the metal ions on the solid phase.

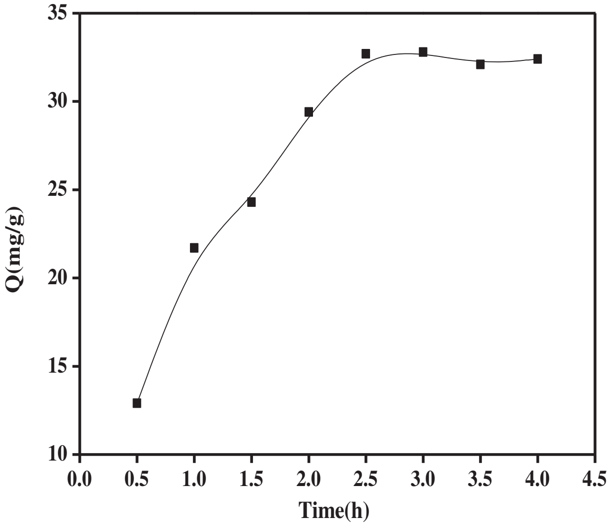


Fig. 5. Adsorption kinetics on the remove of 150 mg/L Sr(II) at pH 7.0, S-IIP amount: 0.4 g, at 25℃, three parallel determinations.

The pseudo-first-order equation was represented by:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \tag{6}$$

where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant q_t is the amount adsorbed at time t (min), and q_e denotes the amount adsorbed at equilibrium, both in mg/g.

The pseudo-second-order equation can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{7}$$

where k_2 (g/(mg min)) is the adsorption rate constant of pseudo-second order.

The linear form of the intra-particle diffusion equation is given by:

$$\ln q_e = \ln k_p + \frac{1}{2} \ln t \tag{8}$$

where k_p ($\mathrm{mg/(g\,min^{1/2})}$) is the intra-particle diffusion rate constant.

The initial adsorption rate (h) can be determined from k_2 and q_e values using:

$$h = k_2 q_e^2 \tag{9}$$

The kinetic parameters are given in Table 1. It can be seen the experimental q_e value (32.60 mg/g) is closed to the calculated value (33.70 mg/g) with 3.4% deviation using pseudo-second order, which does not happen with pseudo-first-order kinetic equation and the intra-particle diffusion kinetic equation. This indicates that the intra-particle diffusion is not the rate-controlling step. Based on the obtained correlation coefficients, the pseudo-second-order equation was the model that furthered the best fits for the experimental kinetic data, suggesting chemical adsorption as the rate-limiting step of the adsorption mechanism and no involvement of a mass transfer in solution. The adsorption of the investigated Sr(II) ions onto S-IIP

Table 1
Pseudo-first, second-order-kinetic, and inter-particle constants determined for Sr(II) adsorption by S-IIP (kinetic studies: 0.4 g sorbent to equilibrate 50 mL of 150 mg L^{-1} Sr(II) solution at pH 7.0, 25℃)

	Pseudo-first order			Pseudo-second order			Inter-particle	
Metal ion	k_1 (min)	q_1 (mg/g)	R	k_2 (g/(mg min))	q_2 (mg/g)	R	k_p (mg/(g $min^{1/2}$))	R
Sr(II)	66.49	40.68	0.9929	6.28×10^{-4}	33.70	0.9984	4.17	0.9580

may consist of two processes with initial adsorption rate of 0.85 mg/(g min).

3.6. Adsorption isotherm

The adsorption isotherm was determined by shaking 50 mg S-IIP with varying concentrations of Sr(II) (2–500 mg/L) at pH 7.0 and 25℃ using the batch procedures. After 2.5 h, the equilibrium concentrations of Sr(II) ions in solution and, consequently, the amounts of the Sr(II) ions bound to the polymer were determined by ICP-AES. From Fig. 6, a relationship was observed between the amount of metal ion adsorbed on the sorbent surface and remaining metal ion concentration in the aqueous phase at equilibrium. It was shown that the adsorption capacity increased with the equilibrium concentration of the metal ion in solution, progressively saturating the sorbent. For interpretation of the adsorption data, the Langmuir, Freundlich isotherm, and Dubinin–Radushkevich isotherm models were used [25–27].

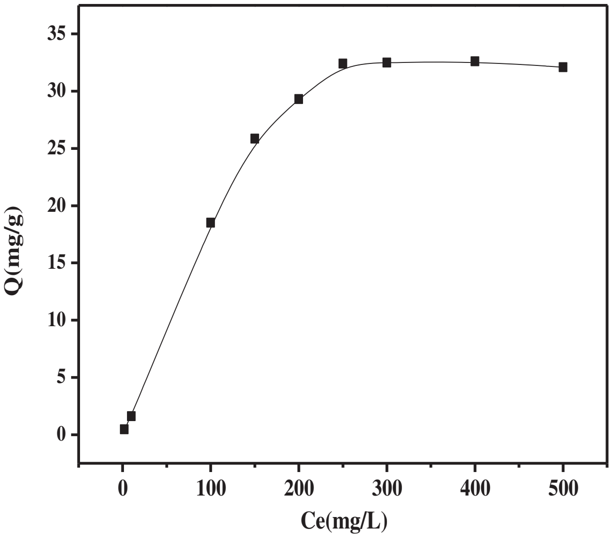


Fig. 6. Adsorption isotherms of Sr(II) ions by S-IIP (Sr(II) concentration: 2–500 mg/L, pH 7.0, S-IIP amount: 0.4 g, contact time: 2.5 h, 25℃, three parallel determinations.

The linear form of the Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{(q_m K_L)} + \frac{C_e}{q_m} \quad (10)$$

where q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration in solution (mg/L), both at equilibrium. K_L (L/mg) is the Langmuir constant and q_m (mg/g) is the maximum adsorption capacity for monolayer formation on sorbent.

The Freundlich equation is given by:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (11)$$

where both K_f and n are constants.

In order to distinguish between physical and chemical adsorption, the equilibrium adsorption data of Sr(II) ions were subjected to the Dubinin–Radushkevich isotherm equation, given by the following equation:

$$\ln q_e = K\varepsilon^2 + \ln q_m \quad (12)$$

where q_e is the amount of metal ions adsorbed (mg/g), q_m is the maximum adsorption capacity of metal ions (mg/g), K is the Dubinin–Radushkevich constant (kJ^2/mol^2), and ε is Polanyi potential given as Eq. (13).

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \quad (13)$$

where C_e is the equilibrium concentration of metal ions (mg/L), R is the gas constant in J/Kmol, and T is the temperate in Kelvin. The Dubinin–Radushkevich constant can give the valuable information regarding the mean energy of adsorption by the following equation:

$$E = (-2K)^{-1/2} \quad (14)$$

where E is the mean adsorption energy (kJ/mol), and K is the Dubinin–Radushkevich constant (kJ^2/mol^2).

The results obtained from adsorption isotherm for Sr(II) by S-IIP are shown in Table 2. For the three studied systems, the Langmuir isotherm correlated better ($R > 0.99$) than Freundlich and Dubinin–Radushkevich isotherm with the experimental data suggested a monolayer adsorption. The maximum adsorption value was 35.33 mg/g, which is very close to the experimentally obtained value (32.60 mg/g). And the Dubinin–Radushkevich adsorption capacity (q_m) was similar to the q_m of the Langmuir adsorption (in Table 2). In addition, the mean adsorption energy (E) from the Dubinin–Radushkevich isotherm is involved the transfer of free energy of one mole of solute from infinity (in solution) to the surface of sorbent. The adsorption behavior might be predicted the physical adsorption in the range of 1–8 kJ/mol of the mean adsorption energies (E), and the chemical adsorption in more than 8 kJ/mol of the mean adsorption energies (E) [28]. The mean adsorption energies (E) of Sr (II) were 15.43 kJ/mol reflected that the adsorption was predominant on the chemisorption process. The Langmuir parameters can be used to predict the affinity between the sorbate and the sorbent using the dimensionless separation factor, RL defined by Dogan et al. [29] as:

$$R_L = \frac{1}{1 + K_L C_0} \tag{15}$$

The values of R_L for adsorption of Sr(II) ions onto S-IIP are 0.956 at 25℃. It indicates a highly favorable adsorption ($R_L < 1$).

Table 2
Langmuir, Freundlich, and Dubinin–Radushkevich isotherm constants (isotherm studies: 50 mg of S-IIP to equilibrate with 50 mL of various concentrations of Sr(II) solutions: 2–500 mg L^{-1}, at pH 7.0, 25℃ for 2.5 h)

Parameter	Adsorption of Sr(II) onto S-IIP
Langmuir isotherm	
q_m (mg/g)	35.33
K_L (L/mg)	0.023
R	0.9966
Freundlich isotherm	
K_f	0.57
n	1.34
R	0.9411
Dubinin–Radushkevich isotherm	
q_m (mg/g)	33.65
K (kJ^2/mol^2)	−0.0021
E (kJ/mol)	15.43
R	0.9487

3.7 Adsorption thermodynamics

The adsorption thermodynamics were necessary to be considered because they can conclude whether the process is spontaneous or not and gain an insight into the adsorption behaviors. The parameters are calculated according to the following thermodynamic equations [30]:

$$K_d = \frac{q_e}{C_e} (\mathrm{L/g}) \tag{16}$$

$$\Delta H^\circ = R \ln \frac{K_d(T_2)}{K_d(T_1)} \times \frac{(T_1 T_2)}{(T_1 - T_2)} (\mathrm{kJ/mol}) \tag{17}$$

$$\Delta G^\circ = -RT \ \ln K_d (\mathrm{kJ/mol}) \tag{18}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} (\mathrm{J/molK}) \tag{19}$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed (mg/g), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). The obtained thermodynamic parameters for Sr(II) sorption onto S-IIP are listed in Table 3. The positive ΔG° values indicated that the adsorption of Sr(II) was non-spontaneous. The number of water molecules surrounding Sr(II) molecules decreased, and the degree of the freedom of water molecules increased by adsorption of abundant Sr(II) onto surface of S-IIP. Therefore, the positive values of ΔS° suggested increased randomness at the solid–solution interface during the adsorption Sr(II) onto the surface of S-IIP. The positive value of enthalpy change ΔH° further confirmed the endothermic nature of the processes, so increasing temperature supplied with a more favorable adsorption.

Table 3
The thermodynamic parameters for Sr(II) S-IIP, sorbent dose: 0.1 g; solution volume: 50.00 mL; solution pH 7.0; contact time: 5 h, at 25℃

Sorbent	T (K)	Thermodynamic parameters		
		ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
S-IIP	298	5.047	12.35	23.94
	318	4.738		
	338	4.250		

Table 4
Adsorption selectivity of S-IIP and NIP (selectivity studies: equilibrating 0.2 g of the surface imprinted polymer or non-ion-imprinted polymer with 50 mL of 4.00 mg L^{-1} Sr(II), 4.00 mg L^{-1} Pb(II), 4.00 mg L^{-1} Ce(III), 4.00 mg L^{-1} Ba(II), 4.00 mg L^{-1} Cs(I), 4.00 mg L^{-1} Ni(II), 4.00 mg L^{-1} Zn(II), and 4.00 mg L^{-1} Co(II) mixture solution, at pH 7.0, 25℃ for 2.5 h)

		A-S-IIP			NIP			
Ions	C_i (mg L^{-1})	C_f (mg L^{-1})	K_d	K	C_f (mg L^{-1})	K_d	K	K'
Sr(II)	4.000	0.084	11,655	—	0.334	2,744	—	—
Pb(II)	4.000	0.103	9,459	1.232	0.172	5,564	0.493	2.499
Ce(III)	4.000	0.152	6,329	1.842	0.231	4,079	0.673	2.737
Zn(II)	4.000	0.243	3,865	3.015	0.370	2,452	1.119	2.694
Cs(I)	4.000	0.699	1,181	9.872	0.782	1,029	2.667	3.702
Ba(II)	4.000	1.300	519	22.446	0.436	2,044	1.343	16.71
Co(II)	4.000	1.495	419	27.823	0.458	1,933	1.419	19.61
Ni(II)	4.000	1.578	384	30.374	0.755	1,075	2.554	11.89

Note: Adsorption selectivity of S-IIP and NIP.

3.8. Selectivity of S-IIP

Selectivity of the S-IIP and NIP was investigated by competitive adsorption of Sr(II), Zn(II), Co(II), Ni (II), Ba(II), Cs(I), Ce(III), and Pb(II) from their mixture. The distribution coefficient (K_d), selectivity coefficient (K), and relative selectivity coefficient (K') are given in Table 4. As can be seen from Table 4, the imprinting effect was clearly observed as S-IIP had a higher adsorption efficiency of Sr(II) than any other metal ions. It indicated that S-IIP has the capability of recognizing Sr(II) with a high affinity and selectivity. Because S-IIP is tailor-made materials with high selectivity for a target Sr(II) ion. Moreover, the relative selectivity coefficients (K') are greater than 1, and this means that Sr(II) ions can be adsorbed more selective than other ions such as Zn(II), Co(II), Ni(II), Ba(II), Cs (I), Ce(III) and Pb(II). As regards to Na(I) and Ca(II), it can be seen from Table 5, the selectivity coefficient (K) of Sr/Na 5.2 and Sr/Ca 14.6 is far more than 1, and it comes to indicate that the prepared surface imprinted polymer could uptake Sr(II) more effectively.

Table 5
Adsorption selectivity of S-IIP toward Na(I) and Ca(II) (selectivity studies: equilibrating 0.2 g of the surface imprinted polymer with 50 mL of 4.00 mg L^{-1} Sr(II), 4.00 mg L^{-1} Na(I), 4.00 mg L^{-1} Ca(II), mixture solution, at pH 7.0, 25℃ for 2.5 h)

Ions	C_0 (mg L^{-1})	C_e (mg L^{-1})	K_d	K
Sr(II)	4.00	0.098	9,954	—
Na(I)	4.00	0.465	1,901	5.2
Ca(II)	4.00	1.074	681	14.6

3.9. Desorption and reusability

After having adsorbed Sr(II) ions, the S-IIP sorbent was desorbed in different concentrations of three acids in Fig. 7. As shown in Fig. 7, by eluting with 1.0 M HNO_3 at 25℃ water bath the desorption ratio was determined to be as high as 99% according to the formula described as Eq. (5). The adsorption–desorption process repeated six times; the adsorption capacity was about 90.6% in the 6th use in Fig. 8. It indicated that the S-IIP can be reused many times without significantly decrease in the adsorption capacity.

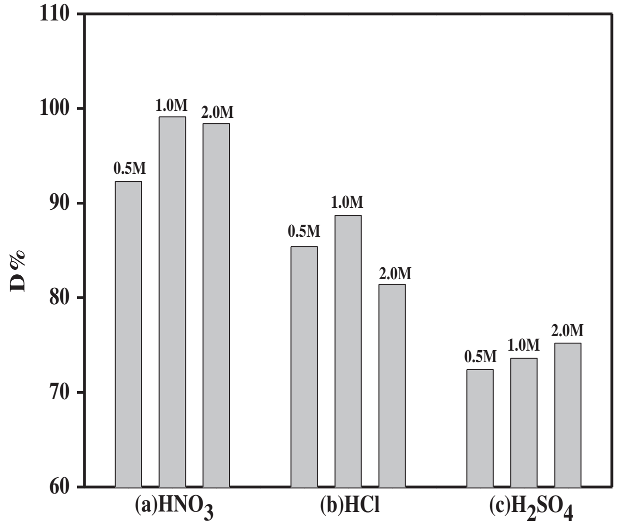


Fig. 7. Desorption of Sr(II) ions from Sr(II) adsorbed onto the S-IIP in different concentrations of HNO_3, HCl, and H_2SO_4, three parallel determinations.

Table 6
Determination and recoveries of Sr(II) in environment water samples ($n = 5$) with the proposed method. (Sample volume: 50 mL, pH 7.0, adsorption: 0.4 g of the S-IIP uptake Sr(II) in sample solutions for 2.5 h at 25℃, desorption: 25 mL 1.0 M HNO_3 at 50℃ water bath for 6 h, three parallel determinations)

Samples	Cs(I) added (μg L^{-1})	Determination (μg L^{-1})	RSD ($n = 5$) (%)	Recovery (%)
Living sewage	0	0.609 ± 0.02	1.28	—
	5.000	5.521 ± 0.03	1.66	110.4
	10.000	10.518 ± 0.03	1.70	105.2
Pond water	0	nd	—	—
	5.000	5.085 ± 0.02	1.81	101.7
	10.000	10.090 ± 0.02	1.98	100.9
Industry waste water	0	0.499±0.02	2.18	—
	5.000	5.493 ± 0.03	1.18	109.8
	10.000	10.501 ± 0.01	1.36	105.0

Note: The value following " ± " is the standard deviation. The nd stands for not find.

3.10. Detection limit and relative standard deviation

The linearity of this method was evaluated using a series of Sr(II) stock solution from 0.050 to 10.000 mg/L. A good linear relationship $y = 8.9736x + 0.0863$ with squared correlation coefficient (r^2) 0.9996 was obtained. The detection limit (3σ) based on three times standard deviations of the blanks by eight replicates was 0.30 μg/L. Measuring 1.0 mg/L of Sr(II) 10 times, the relative standard deviation (RSD) for 1.0 mg/L Sr(II) was 0.93%.

3.11. Application of the method

In order to evaluate the feasibility of the proposed method, it was applied to the analysis of cesium in several water samples. For the analysis of these water samples, the standard addition method was used. As is shown in Table 6, the recoveries of Sr(II) were in the range of 101.7–110.4%. These results indicated the suitability of this method for selective SPE and determination of trace Sr(II) in environmental samples.

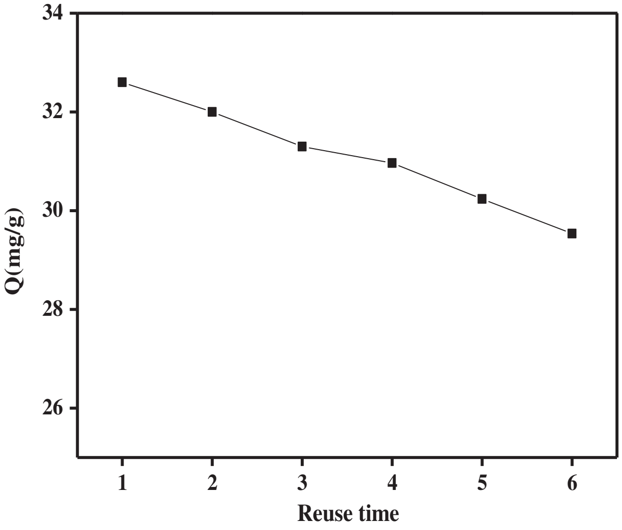


Fig. 8. Reuse of S-IIP.

4. Conclusions

The prepared S-IIP finds broad application as selective SPE for trace Sr(II) ions from aqueous solutions. Through a series of adsorption experiments educed a high adsorption capacity of 32.60 mg/g under the optimum conditions, and a fast initial adsorption rate of 0.85 mg/(g min). The selectivity experiments showed that S-IIP had a higher selectivity of Sr(II) than NIP and the relative selectivity coefficients (K') are greater than 1. In addition, the dynamical study showed to be well followed the pseudo-second-order kinetic equation in the adsorption process. At the same time, the equilibrium adsorption studies was fitted in three adsorption isotherm models, namely, Langmuir, Freundlich, and Dubinin–Radushkevich to show very good fits in the Langmuir isotherm equation for the monolayer adsorption process. The thermodynamic analysis presented the endothermic, non-spontaneous, and entropy gained nature of the adsorption process. The method was successfully applied to the analysis of trace Sr(II) in wastewater samples.

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References

[1] S. García-Ruiz, M. Moldovan, G. Fortunato, S. Wunderli, J.I.G. García Alonso, Evaluation of strontium isotope abundance ratios in combination with multi-elemental analysis as a possible tool to study the geographical origin of ciders, Anal. Chim. Acta 590 (2007) 55–66.

[2] N.M. Kocherginsky, Y.K. Zhang, J.W. Stucki, D2EHPA based strontium removal from strongly alkaline nuclear waste, Desalination 144 (2002) 267–272.

[3] K. Roy, P.K. Mohapatra, N. Rawat, D.K. Pal, S. Basu, V.K. Manchanda, Separation of 90Y from 90Sr using zirconium vanadate as the ion exchanger, Appl. Radiat. Isot. 60 (2004) 621–624.

[4] J.E. Roane, T.A. Devol, J.D. Leyba, R.A. Fjeld, The use of extraction chromatography resins to concentrate actinides and strontium from soil for radiochromatographic analyses, J. Environ. Radioact. 66 (2003) 227–245.

[5] R.A. Shawabkeh, D.A. Rockstraw, R.K. Bhada, Copper and strontium adsorption by a novel carbon material manufactured from pecan shells, Carbon 40 (2002) 781–786.

[6] N. Rajesh, B. Deepthi, A. Subramaniam, Solid phase extraction of chromium(VI) from aqueous solutions by adsorption of its ion-association complex with cetyltrimethylammonium bromide on an alumina column, J. Hazard. Mater. 144 (2006) 464–469.

[7] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. 97 (2003) 219–243.

[8] M. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads, J. Hazard. Mater. 93 (2002) 233–248.

[9] S. Sadeghi, A.A. Mofrad, Synthesis of a new ion imprinted polymer material for separation and preconcentration of traces of uranyl ions, React. Funct. Polym. 67 (2007) 966–976.

[10] R. Kala, J.M. Gladis, T.P. Rao, Preconcentrative separation of erbium from Y, Dy, Ho, Tb and Tm by using ion imprinted polymer particles via solid phase extraction, Anal. Chim. Acta 518 (2004) 143–150.

[11] X. Chang, N. Jiang, H. Zheng, Q. He, Z. Hu, Y. Zhai, Y. Cui, Solid-phase extraction of iron(III) with an ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique, Talanta 71 (2007) 38–43.

[12] V.M. Biju, J.M. Gladis, T.P. Rao, Ion imprinted polymer particles: Synthesis, characterization and dysprosium ion uptake properties suitable for analytical applications, Anal. Chim. Acta 478 (2003) 43–51.

[13] Z. Zhang, X. Xu, Y. Yan, Kinetic and thermodynamic analysis of selective adsorption of Cs(I) by a novel surface whisker-supported ion-imprinted polymer, Desalination 263 (2010) 97–106.

[14] T.P. Rao, R. Kala, S. Daniel, Metal ion-imprinted polymers—Novel materials for selective recognition of inorganics, Anal. Chim. Acta 578 (2006) 105–116.

[15] F. Vandevelde, J. Pantigny, I. Pezron, L.A. Gheber, K. Haupt, Nanostructured molecularly imprinted polymer films as synthetic recognition layers, Int. J. Nanotechnol. 5 (2008) 757–768.

[16] R.S. Praveen, S. Daniel, T.P. Rao, Solid phase extraction preconcentration of cobalt and nickel with 5,7-dichloroquinone-8-ol embedded styrene–ethylene glycol dimethacrylate polymer particles and determination by flame atomic absorption spectrometry (FAAS), Talanta 66 (2005) 513–520.

[17] E. Birlik, A. Ersöz, A. Denizli, R. Say, Preconcentration of copper using double-imprinted polymer via solid phase extraction, Anal. Chim. Acta 565 (2006) 145–151.

[18] M. Tuzen, M. Soylak, Multiwalled carbon nanotubes for speciation of chromium in environmental samples, J. Hazard. Mater. 147 (2007) 219–225.

[19] T.P. Rao, S. Daniel, J.M. Gladis, Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIP-SPE), Trends Anal. Chem. 23 (2004) 28–35.

[20] L.M. Zhou, Y.P. Wang, Z.R. Liu, Q.W. Huang, Characteristics of equilibrium, kinetics studies for adsorption of Hg(II), Cu(II), and Ni(II) ions by thiourea-modified magnetic chitosan microspheres, J. Hazard. Mater. 161 (2009) 995–1002.

[21] Y.G. Tao, L.B. Ye, J. Pan, Y.M. Wang, B. Tang, Removal of Pb(II) from aqueous solution on chitosan/TiO_2 hybrid film, J. Hazard. Mater. 161 (2009) 718–722.

[22] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–742.

[23] M. Yurdakoç, Y. Seki, S.K. Karahan, Kinetic and thermodynamic studies of boron removal by Siral 5, Siral 40, and Siral 80, J. Colloid Interface Sci. 286 (2005) 440–446.

[24] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal Ions on chitosan, Water Res. 35 (2001) 613–618.

[25] C. Niu, W. Wu, Z. Wang, S. Li, J. Wang, Adsorption of heavy metal ions from aqueous solution by cross-linked carboxymethyl konjac glucomannan, J. Hazard. Mater. 141 (2007) 209–214.

[26] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies for the sorption of lead from effluents using chitosan, Chemosphere 52 (2003) 1021–1030.

[27] S.P. Ramnani, S. Sabharwal, Adsorption behavior of Cr(VI) onto radiation crosslinked chitosan and its possible application for the treatment of wastewater containing Cr(VI), React. Funct. Polym. 66 (2006) 902–909.

[28] M. Doğan, M. Alkan, Removal of methyl violet from aqueous solution by perlite, J. Colloid Interface Sci. 267 (2003) 32–41.

[29] A.H. Chen, S.C. Liu, C.Y. Chen, C.Y. Chen, Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin, J. Hazard. Mater. 154 (2008) 184–191.

[30] A.E. Ofomaja, Intraparticle diffusion process for lead (II) biosorption onto mansonia wood sawdust, Bioresour. Technol. 101 (2010) 5868–5876.