

## Selective removal of iron from aqueous solution using ion imprinted thiocyanato-functionalized silica gel sorbents

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**Abstract**—We combined surface imprinting technique with sol-gel process for preparing a new iron(III)-imprinted thiocyanato-functionalized silica gel sorbent using 3-thiocyanatopropyltriethoxysilane as the functional monomer, and epichlorohydrin as the cross-linking agent for the selective removal of iron(III) from aqueous solution. The iron(III)-imprinted thiocyanato-functionalized silica gel was characterized by FT-IR spectra, SEM, and the static adsorption-desorption method. Maximum binding capacity, optimum pH, and equilibrium binding time were found to be 20.31 mg·g<sup>-1</sup>, pH 4.2, and 20 min, respectively. The relative selectivity coefficients of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbents for Fe(III)/Ni(II), Fe(III)/Co(II), Fe(III)/Cd(II) and Fe(III)/Pb(II) were 11.8, 10.6, 8.2 and 9.1 times greater than the non-imprinted silica gel, respectively. The iron(III)-imprinted thiocyanato-functionalized silica gel sorbents could be used repeatedly without decreasing in their adsorption capacities significantly.

Key words: Iron, Sol-gel, 3-Thiocyanatopropyltriethoxysilane, Ion Imprinted Polymer

### INTRODUCTION

Although iron is an essential mineral, its presence in drinking water and water supplies causes problems, such as discoloration, metallic taste, odor, turbidity, and staining of laundry and plumbing fixtures. Iron oxides, which are formed in reservoirs upon aerial oxidation of dissolved iron, also promote the growth of micro-organisms in water [1]. Thus, the World Health Organization has set a guideline value of 0.3 mg·L<sup>-1</sup> of iron in drinking water [2].

The conventional method for the removal of iron from solution involves hydroxide precipitation, filter, electrocoagulation, and ion exchange techniques [3-6]. Adsorption, which is one of the most important physicochemical processes that occur at the solid-liquid and solid-gas interfaces, has become an effective and economical method with a high potential for the removal, recovery and recycling of toxic heavy metals from wastewater [7].

Molecular imprinting is a state-of-the-art technique for imparting molecular recognition properties to a synthetic polymeric matrix. Molecular imprinting is a process whereby functional and cross-linking monomers are co-polymerized in the presence of the target analyte (the imprint molecule), which acts as a molecular template. The functional monomers initially form a complex with the imprint molecule and following polymerization. Their functional groups are held in position by the highly cross-linked polymeric structure. Subsequent removal of the imprint molecule reveals binding sites that are complementary in size and shape to the analyte. In that way, a molecular memory is introduced into the polymer, which is called as molecular imprinting polymer capable of rebinding the analyte with a very high specificity [8]. Ion imprinted polymers (IIPs) are similar to molecular imprinting polymer, but they can recognize

metal ions after imprinted and retain all of the virtue of molecular imprinting polymer [9,10]. Conventionally, the imprinted technique is easily carried out using bulk imprinting, where imprinted polymers are prepared in large chunks, and post-treatment processes like grinding and sieving are then required. However, the creation of binding sites within the polymeric bulk and the issue of the hindrance of adsorbate diffusion during template rebinding limit the imprinted polymers prepared for the practical applications [11]. Thus, over the years many efforts to address the limitations of conventional imprinting techniques have resulted in new imprinting methodologies. Surface imprinting is one of the important imprinting methods. Surface imprinted polymers not only possess high selectivity but also avoid problems with mass transfer, and shows significant promise for the industrial applications [11,12].

However, a few Fe(III) surface imprinted sorbents have been reported. Chang et al. [13] prepared a Fe(III)-imprinted amino-functionalized silica gel sorbent using the surface imprinting method. Karabörk et al. [14] reported an intersurface Fe(III)-imprinted nanocomposites polymer with high selectivity for Fe(III) ions. Owens et al. [15] prepared a Fe(III)-imprinted ion-exchange resin for the selective adsorption of Fe(III). In this study, a new Fe(III)-imprinted thiocyanato-functionalized silica gel sorbent was synthesized by combining a surface molecular imprinting technique with a sol-gel process for the selective removal of Fe(III) from aqueous solutions. The synthesis, characterization, kinetics of adsorption and desorption, and the selectivity of this new sorbent were discussed.

### MATERIALS AND METHODS

#### 1. Materials and Apparatus

Silica gel (80-120 mesh) was purchased from Qingdao Ocean Chemical Co., Qingdao, China. 3-Thiocyanatopropyltriethoxysilane (TCPTS) was obtained from Jingzhou Jiangnan Fine Chemical Co.,

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Ltd., Hubei, China. All the other reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Shanghai, China. All solutions were prepared using double-distilled water. Fe(III) readily forms Fe(OH)<sub>3</sub> even at fairly low pH. Concentrated solutions of Fe(III) from FeCl<sub>3</sub> were readily prepared by dissolving the salt in water and were maintained at a relatively low pH < 3.5 for avoiding solid matter accumulating on the bottom of the flasks.

FT-IR spectra (4,000–450 cm<sup>-1</sup>) with KBr pellets and a resolution of 1 cm<sup>-1</sup> were recorded using a Spectrum One spectrometer (Perkin Elmer, USA). The surface morphology of the Fe(III)-imprinted sorbents was examined using scanning electron microscopy (SEM, Shimadzu Corporation, Japan). The concentrations of Fe(III), Cd(II), Co(II), Ni(II) and Pb(II) in aqueous solutions were determined by an AA-700 flame atomic absorption spectrometer (FAAS, Perkin Elmer, USA). A pH-S-3C digital pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) was used for the pH adjustments.

## 2. Preparation

The silica gel (15 g) was mixed in 120 mL of 33% methanesulfonic acid in a covered beaker, and held in a water bath under stirring for 8 h. The mixture was refluxed for 24 h in a dry atmosphere. After acid treatment, the acid-activated silica gel was filtered, consecutively washed with doubly deionized water to neutral, and dried under high vacuum at 303.15 K.

6 mL of TCPTS and 4.55 g of FeCl<sub>3</sub>·6H<sub>2</sub>O were dissolved in 200 mL of methanol under stirring and heating for 2 h. In a 500 mL round-bottomed flask, equipped with a mechanical stirrer, a thermometer, and a reflux condenser, 12 g acid-activated silica gel was added. The mixture was reacted for 24 h at 303.15 K. 8 mL of epichlorohydrin was added at 303.15 K for 2 h. After the copolymerization, the contents of the flask were recovered by filtration, washed with ethanol, and stirred in 50 mL of 6 mol·L<sup>-1</sup> HCl for 2 h. The final product was recovered by filtration, washed with doubly deionized water up to the eluent pH=5–6 and dried under vacuum at 303.15 K for 24 h. For comparison, the non-imprinted sorbents were also prepared similarly to the iron(III)-imprinted sorbents, but without using FeCl<sub>3</sub>·6H<sub>2</sub>O.

## 3. Characterization

The FT-IR spectra of the iron(III)-imprinted sorbents silica gel sorbents were recorded with KBr pellets and a resolution of 1 cm<sup>-1</sup>. The surface of the sample was characterized by SEM at the desired magnification to study the morphology of the Fe(III)-imprinted sorbents.

## 4. Adsorption and Desorption Tests of Iron(III)

Adsorption of Fe(III) from aqueous solutions was investigated in a batch experiment. The uptake of Fe(III) from solution by iron(III)-imprinted sorbents was fairly rapid. In a typical uptake kinetics test, 50 mg of the imprinted sorbent was added to 25 mL of the solutions containing 300 mg·L<sup>-1</sup> Fe(III) solution at a pH of 4.2. The suspension was stirred for different periods of time (from 5 to 60 min). The effect of pH on the static adsorption of Fe(III) was tested by equilibrating 50 mg of iron(III)-imprinted sorbent with 25 mL of the solutions containing 300 mg·L<sup>-1</sup> of Fe(III) under different pH conditions. The suspensions were brought to the desired pH by adding sodium hydroxide and nitric acid. To measure the static adsorption capacity, 50 mg of iron(III)-imprinted sorbent was equilibrated with 25 mL of various concentrations (5–500 mg·L<sup>-1</sup>) of Fe(III) solu-

tions at pH 4.2. The influence of stripping agents on the desorption of iron(III)-imprinted sorbents for Fe(III) was also investigated. Several stripping agents, including EDTA, HNO<sub>3</sub>, and HCl, were used to remove the adsorbed Fe(III) from the sorbents at a rate of 600 rpm. The desorption ratio was calculated from the amount of Fe(III) ions adsorbed on the sorbents and the final Fe(III) ion concentration in the desorption medium. In all the above batch experiments, the mixtures were stirred at room temperature, then centrifugally separated under 3,000 rpm for 5 minutes. The supernatants were measured for unextracted metal ions by FAAS. The experiments were performed in replicates of three, and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples to determine the margin of error.

## 5. Selectivity Experiments

To show the selectivity, the binary competitive binding ability of Cd(II), Pb(II), Co(II) and Ni(II) with respect to Fe(III) was studied. 50 mg of iron(III)-imprinted or non-imprinted sorbent was added in 25 mL of 50 mg·L<sup>-1</sup> binary metal (Fe(III)/Ni(II), Fe(III)/Co(II), Fe(III)/Cd(II) and Fe(III)/Pb(II)) mixed solutions at pH 4.2. The distribution and selectivity coefficients of Cd(II), Pb(II), Co(II) and Ni(II) with respect to Fe(III) can be obtained from equilibrium binding data according to Eqs. (1) and (2).

$$K_d = [(C_i - C_f)/V]m \quad (1)$$

In Eq. (2),  $K_d$  represents the distribution coefficient;  $C_i$  and  $C_f$  are the initial and final concentrations of metal ions (mg·L<sup>-1</sup>), respectively.  $V$  is the volume of the solution (mL);  $m$  is the mass of sorbents used (g).

$$k = K_d(\text{Fe}^{3+})/K_d(\text{X}^{2+}) \quad (2)$$

$k$  is the selectivity coefficient, and  $\text{X}^{2+}$  represents Cd(II), Pb(II), Co(II) and Ni(II) ions. A comparison of the  $k$  values of iron(III)-imprinted or non-imprinted sorbents with those metal ions allows an estimation of the effect of imprinting on selectivity.

A relative selectivity coefficient  $k'$  (Eq. (3)) can be defined as

$$k' = k_{\text{imprinted}}/k_{\text{non-imprinted}} \quad (3)$$

## 6. Reusability

To test the reusability of the iron(III)-imprinted sorbents, the Fe(III) ion adsorption-desorption procedure was repeated six times by using the same sorbents. The metal ions were removed from the sorbents by washing with 15 mL of 3 mol·L<sup>-1</sup> HCl for 1 h. The sorbents were rinsed several times with deionized water and then neutralized to pH 7 using 0.1 mol·L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> solution for up to 24 h to ensure complete H<sup>+</sup> neutralization. The sorbents were washed again with deionized water and dried under vacuum at 303.15 K overnight before another extraction cycle.

# RESULTS AND DISCUSSION

## 1. Synthesis of Iron(III)-imprinted Thiocyanato-functionalized Silica Gel Sorbents

Silica gel is an amorphous inorganic polymer with siloxane groups (Si-O-Si) in the bulk and silanol groups (Si-OH) on its surface. The latter are responsible for chemical modifications that may occur on

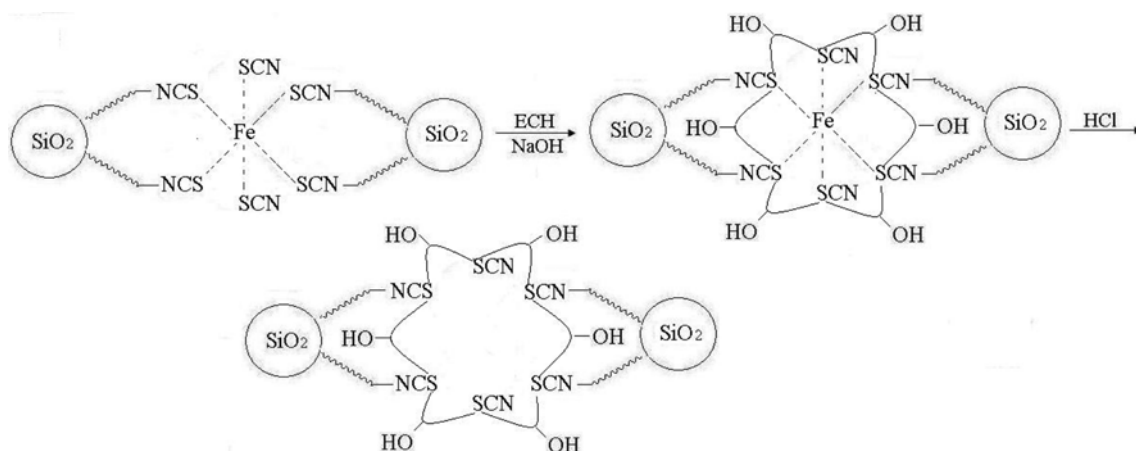


Fig. 1. Preparation procedure of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbents.

the silica surface. Because commercial silica gel possesses a low concentration of surface silanol groups suitable for modification, the activation of silica gel surfaces is necessary. The previous research reported that methanesulfonic acid with good properties is used for the activation of the silica gel [12]. In this work, silica gel was also activated by 33% methanesulfonic acid solution. A complex was formed between Fe(III) and TCPTS, then co-hydrolyzed and co-condensed with the activated silica gel. Thus, the activated silica gel surface was grafted with the complex of Fe(III) and TCPTS rather than just the free TCPTS. After the remnant TCPTS and Fe(III) were removed by ethanol and 6 mol L<sup>-1</sup> HCl, respectively, the imprinted silica gel sorbents which contained a tailor-made cavity for Fe(III) were formed. Fig. 1 shows the preparation process of iron(III)-imprinted thiocyanato-functionalized silica gel sorbents.

## 2. Characterization of Iron(III)-imprinted Thiocyanato-functionalized Silica Gel Sorbents

To confirm the presence of TCPTS in the iron(III)-imprinted sorbents, the FTIR spectra of silica gel and iron(III)-imprinted sorbents are shown in Fig. 2. Compared with silica gel, the spectral features of TCPTS in iron(III)-imprinted sorbents were obtained. The presence of OH groups is reflected by vibration band at 3,445 cm<sup>-1</sup> and at 1,635 cm<sup>-1</sup> due to the surface silanol groups with hydrogen bond and the remaining adsorbed water molecules [16]. The

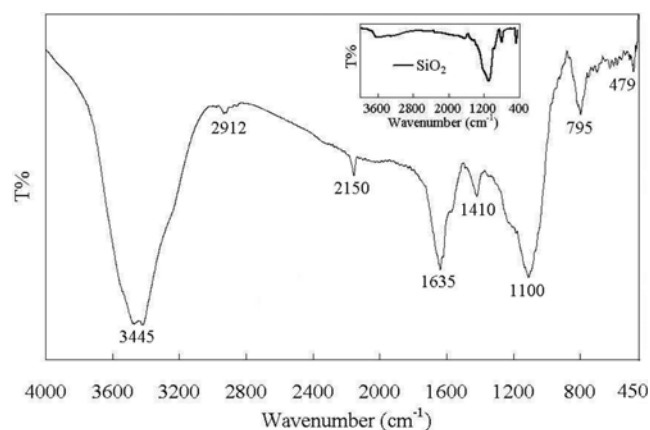


Fig. 2. IR spectra of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbents and silica gel.

presence of CH<sub>2</sub> groups is reflected by vibration band at 2,912 cm<sup>-1</sup>. The absorption band at 2,150 cm<sup>-1</sup> is assigned to C=N vibrations of thiocyanato groups [17,18]. A broad peak is noted at 1,100 cm<sup>-1</sup>, due to the siloxane vibrations of (SiO)<sub>n</sub> [19]. Other bands at 795 cm<sup>-1</sup> and 479 cm<sup>-1</sup> are assigned to Si-O-Si stretching and Si-O-Si bending, respectively [20]. The band at 1,410 cm<sup>-1</sup> corresponds to  $\delta(\text{N-CH}_2)$  [19]. These results indicated that TCPTS had been successfully immobilized onto the surface of silica gel.

The rough surface morphology and microporous interior of iron (III)-imprinted sorbents were exemplified by the scanning electron micrographs. Fig. 3 presents the morphological difference of iron(III)-imprinted (Fig. 3(a)) and non-imprinted (Fig. 3(b)) sorbents. However, there are obviously some holes existing within the iron(III)-imprinted sorbents. These strongly indicate that a template imprint was formed within iron(III)-imprinted sorbents. Regarding the difference of two sorbents, it is important to mention the general role Fe(III) ion plays in the preparation of iron(III)-imprinted sorbents. Assembled with metal as the pivot, as already explained, monomers were regularly positioned around the templates via a coordinating bridge. Since the coordination bond was stronger than the hydrogen bond used in iron(III)-imprinted sorbents, the relative motion of monomer-template was largely restricted. After polymerization and removing the template, the imprint with a relative higher fidelity was thus left behind. As a result, the prepared iron(III)-imprinted sorbents, in logic, could be expected to show a better recognition toward the imprint Fe(III) ion.

## 3. Effects of pH

The effects of the initial pH of solutions on Fe(III) adsorption are shown in Fig. 4. As seen here, the adsorption capacity of Fe(III) was very low when the pH was lower than pH 2.7 because of the protonation, but it increased dramatically with the increase of pH in range from 2.7 to 4.2. After pH 4.2, the adsorption capacity remained relatively constant. To avoid hydrolyzing at higher pH values, the adsorption of Fe(III) ion should be achieved at pH 4.2 for all the experiments.

## 4. Kinetic Curve of Adsorption Rate

The uptake of Fe(III) from solution by Fe(III)-imprinted sorbents was fairly rapid. Fig. 5 shows the time dependence of the adsorption capacity of imprinted sorbents for Fe(III) ions. It can be seen from Fig. 5 that the adsorption of Fe(III) ions is initially fast,

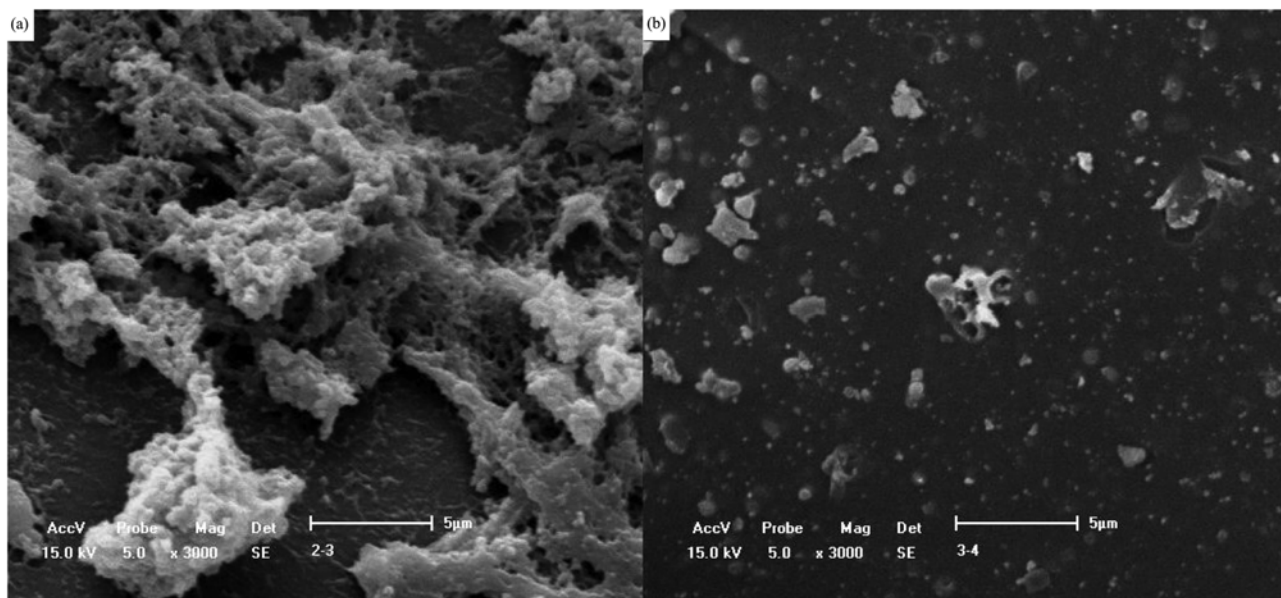


Fig. 3. SEM of Fe(III)-imprinted thiocyanato-functionalized silica gel and non-imprinted sorbents.

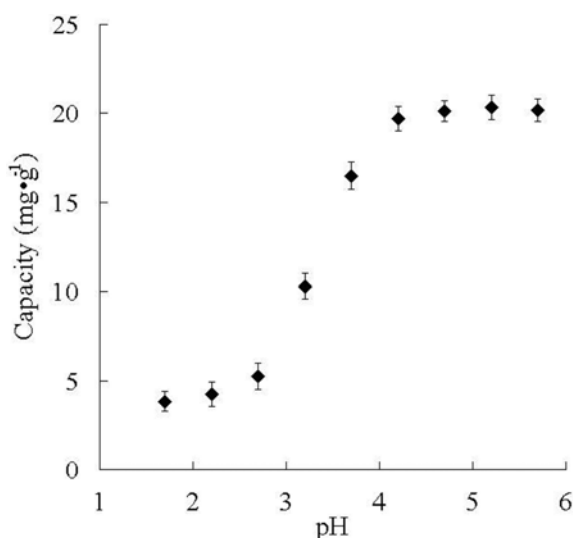


Fig. 4. Effect of pH on the adsorption capacity of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbents for Fe(III): Concentration of Fe(III)=300 mg·L<sup>-1</sup>, temperature=293.15 K.

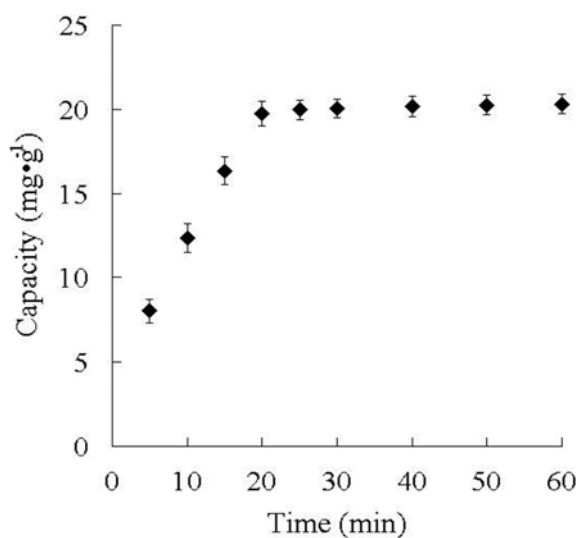


Fig. 5. Adsorption rates of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbents for Fe(III): Concentration of Fe(III)=300 mg·L<sup>-1</sup>, pH=4.2, temperature=293.15 K.

with the most iron(III) being adsorbed within the first few minutes, and a complete equilibrium between the two phases is established in 20 min. This fast adsorption equilibrium is due to the smaller diffusion barrier of imprinted sorbent which was prepared by surface imprinting technique for Fe(III) ions.

Two different kinetic models (the pseudo-first-order and pseudo-second-order kinetic models) were used to fit the experimental data.

The formula of pseudo-first-order kinetic model for the adsorption of solid/liquid systems is given as [21]:

$$dq_{eq}/dt = k_1(q_{eq} - q) \quad (4)$$

After integration with the initial condition  $q=0$  at  $t=0$ , Eq. (4) can be obtained

$$q = q_{eq}(1 - \exp^{-k_1 t}) \quad (5)$$

It can be represented in a linear expression as Eq. (6)

$$\log(q_{eq} - q) = \log q_{eq} - k_1 t / 2.303 \quad (6)$$

where  $q$  is the adsorption capacity at time  $t$  (mg·g<sup>-1</sup>) and  $k_1$  (min<sup>-1</sup>) is the rate constant of the pseudo-first adsorption. The rate constant,  $k_1$  and correlation coefficients were calculated from the linear plots of  $\log(q_{eq} - q)$  versus  $t$  and listed in Table 1. A low correlation coefficient of pseudo-first-order kinetic model for Fe(III)-imprinted sorbents was observed, indicating a poor pseudo-first-order fit to the experimental data.

The kinetic data were further analyzed using Ho's pseudo-sec-

**Table 1. Comparison of the pseudo-first and pseudo-second-order constants**

$q_{eq}$ (exp) (mg g <sup>-1</sup> )	Pseudo-first-order model			Pseudo-second-order model		
	$k_1$ (min <sup>-1</sup> )	$q_{eq}$ (cal) (mg·g <sup>-1</sup> )	$r^2$	$k_2$ ( $\times 10^{-3}$ g·mg <sup>-1</sup> ·min <sup>-1</sup> )	$q_{eq}$ (cal) (mg·g <sup>-1</sup> )	$r^2$
20.31	0.035	8.71	0.6725	7.18	22.99	0.9901

ond-order kinetics model. This model is based on the assumption the sorption follows second-order chemisorptions [22]. It can be expressed as Eq. (7):

$$dq_{eq}/dt = k_2(q_{eq} - q)^2 \quad (7)$$

When the initial condition is  $q=0$  at  $t=0$ , integration leads to Eq. (8):

$$q = k_2 q_{eq}^2 t / (1 + k_2 q_{eq} t) \quad (8)$$

It can be represented in a linear expression from the linear plots of  $t/q$  against  $t$  as Eq. (9)

$$t/q = 1/k_2 q_{eq}^2 + t/q_{eq} \quad (9)$$

where  $k_2$  (g·mg<sup>-1</sup>·min<sup>-1</sup>) is the rate constant of the pseudo-second-order adsorption. The rate constant  $k_2$ , the  $q_{eq}$  value and the corresponding linear regression correlation coefficient  $r^2$  were calculated from the linear plots of  $t/q$  against  $t$  and given in Table 1. The values of  $q_{eq}$  (cal), and  $k_2$  for Fe(III)-imprinted sorbents were 22.99 mg·g<sup>-1</sup> and  $7.2 \times 10^{-3}$  g·mg<sup>-1</sup>·min<sup>-1</sup>, respectively. A straight line with extremely high correlation coefficients ( $r^2=0.9901$ ) was obtained. In addition, the calculated  $q_{eq}$  values also agreed with the experimental data in the case of pseudo-second-order kinetics. These results suggest that the adsorption data of Fe(III)-imprinted sorbents was well represented by pseudo-second-order kinetics model and the rate-limiting step of Fe(III) onto Fe(III)-imprinted sorbents may be chemical sorption or chemisorptions.

## 5. Adsorption Capacity

The adsorption capacity is an important factor to evaluate the

imprinted sorbents because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. Fig. 6 shows the initial concentrations of Fe(III) ions dependence of the adsorbed amount of Fe(III) onto the Fe(III)-imprinted sorbents. As can be seen, the values of adsorption capacity of Fe(III)-imprinted sorbents increase with the increase of the initial concentration of Fe(III) in the range from 5 to 300 mg·L<sup>-1</sup>, and the adsorption capacity reaches a saturation value at initial Fe(III) ion concentration of 300 mg·L<sup>-1</sup>, which represents saturation of the active binding cavities on the Fe(III)-imprinted sorbents. The experimental values of the maximum static adsorption capacity of the Fe(III)-imprinted sorbents and NIP sorbents were 20.31 and 9.58 mg·g<sup>-1</sup>, respectively. The maximum static adsorption capacity of Fe(III)-imprinted sorbents was 2.1 times as much as that of non-imprinted sorbents.

The data obtained were converted to Langmuir and Freundlich isotherms. The Langmuir model assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. The Langmuir model can be described by the equation [23],

$$q_e = q_{max} b C_e / (1 + b C_e) \quad (10)$$

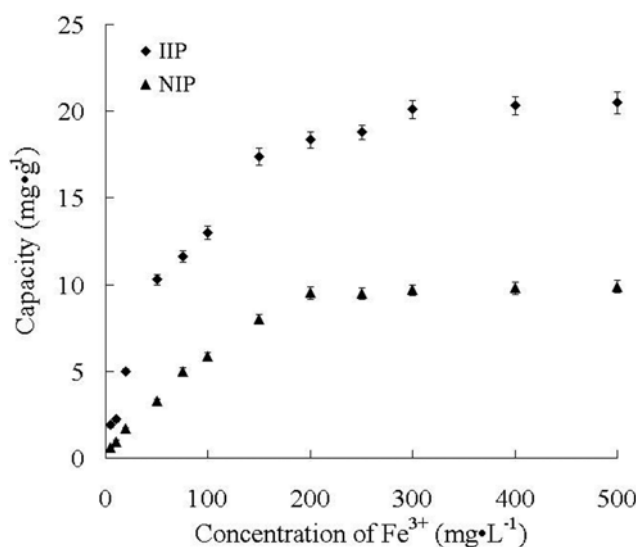
where  $q_e$  is the amount of adsorbed Fe(III) in the Fe(III)-imprinted sorbents (mg·g<sup>-1</sup>),  $C_e$  is the equilibrium ion concentration in solution (mg·L<sup>-1</sup>),  $b$  is the Langmuir constant (L·mg<sup>-1</sup>), and  $q_{max}$  is the maximum adsorption capacity (mg·g<sup>-1</sup>).

The Freundlich expression is an exponential equation that describes reversible adsorption and is not restricted to the formation of the monolayer. This empirical equation takes the form [24],

$$q_{eq} = K_F C_{eq}^{1/n} \quad (11)$$

where  $K_F$  and  $n$  are the Freundlich constants;  $C_{eq}$  is the equilibrium ion concentration in solution (mg·L<sup>-1</sup>).

According to the literature, which states that the values of  $R^2$  are regarded as a measurement of the goodness-of-fit of experimental data on the isotherm models [22,23], for the systems considered, the Langmuir model ( $R^2=0.9959$ ) was found to be more applicable than the Freundlich model ( $R^2=0.9647$ ) in interpreting Fe(III) adsorption on the Fe(III)-imprinted sorbents. Table 2 shows the kinetic constants of the Langmuir and Freundlich isotherms. The calculation value of maximum adsorption capacity ( $q_{max}$ ) of Fe(III)-imprinted sorbents for Fe(III) ions was 22.03 mg·g<sup>-1</sup>. There was a low difference of  $q_{max}$  between the experiment and calculation values.



**Fig. 6. Adsorption capacity of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbents for Fe(III): pH=4.2, temperature=293.15 K.**

**Table 2. Constants of Langmuir and Freundlich isotherms**

Langmuir adsorption isotherm	Freundlich adsorption isotherm
$q_{max}=22.03$ mg·g <sup>-1</sup>	$K_F=1.86$
$b=0.030$ L·mg <sup>-1</sup>	$n=2.31$
$R^2=0.9959$	$R^2=0.9647$

**Table 3. The selectivity parameters of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbents for Fe(III)**

Metals	Sorbents	$K_d$		k	k'
		$K_d$ (Fe)	$K_d$ (X)		
Fe(III)/Co(II)	IIP	4362	140	31.16	10.6
	NIP	2712	920	2.95	
Fe(III)/Ni(II)	IIP	3494	238.8	14.63	11.8
	NIP	1062	855.6	1.24	
Fe(III)/Cd(II)	IIP	4208	142	30.09	8.2
	NIP	1912	520	3.68	
Fe(III)/Pb(II)	IIP	4362	178	24.93	9.1
	NIP	2472	900	2.75	

## 6. Selective Adsorption

Competitive adsorptions of Fe(III)/Ni(II), Fe(III)/Co(II), Fe(III)/Cd(II) and Fe(III)/Pb(II) were investigated in their double mixture system. Table 3 summarizes  $K_d$ , k, and k' values of Cd(II), Pb(II), Co(II) and Ni(II) with respect to Fe(III). The relative selectivity coefficient is an indicator to express metal adsorption affinity of recognition sites to the imprinted iron(III) ions. The ion imprinting effect was clearly observed by comparing the selectivity results of iron(III)-imprinted or non-imprinted sorbents in terms of relative selectivity coefficients (k'). These results showed that the relative selectivity coefficients of the imprinted sorbents for Fe(III)/Ni(II), Fe(III)/Co(II), Fe(III)/Cd(II) and Fe(III)/Pb(II) were, respectively, 11.8, 10.6, 8.2 and 9.1 times greater than for non-imprinted sorbent. A significant difference between the binding of Fe(III) and other competitor metal ions to the imprinted sorbent clearly suggested that high complexation and geometric affinity between Fe(III) ions and cavities of Fe(III) in the imprinted sorbent structure played an essential role in the selective binding of the imprinted sorbents for Fe(III).

## 7. Desorption and Repeated Use

The regeneration of the imprinted sorbent is likely to be a key factor in improving wastewater process economics. In this study, desorption of the adsorbed Fe(III) ions from the imprinted sorbent was also studied in a batch experimental set-up. The 10 mL of 3 mol·L<sup>-1</sup> HCl solution was found to be quite effective for removing the adsorbed Fe(III) from the sorbents. The desorption time was found to be 2 h. With a single wash of 3 mol·L<sup>-1</sup> of HCl solution, desorption ratios were very high (up to 94.5%). It was most possibly due to the complete protonation of donating atoms of binding sites in the cavities of the imprinted sorbents, when 3 mol·L<sup>-1</sup> of HCl solution penetrated into the polymeric network.

To show the reusability of the Fe(III)-imprinted sorbent, the adsorption-desorption cycle was repeated five times using the same imprinted sorbents. After five repeated adsorption-desorption cycles, the adsorption capacity of Fe(III)-imprinted sorbent was decreased about 9% and the same sample of the sorbent was found to remove 90% of Fe(III) from solution. The results showed that the Fe(III)-imprinted sorbent could be used repeatedly without losing their adsorption capacities significantly.

## CONCLUSIONS

A new selective sorbent for the removal of iron was developed

using the combination of surface imprinting technique with a sol-gel process making Fe(III)-imprinted thiocyanato-functionalized silica gel. The preparation of Fe(III)-imprinted thiocyanato-functionalized silica gel sorbent was relatively simple and rapid. The Fe(III)-imprinted thiocyanato-functionalized silica gel sorbent had high adsorption capacity, fast adsorption rates, and high selectivity for Fe(III) due to the unique size and shape of active binding cavities of Fe(III) on its surface. The Fe(III)-imprinted sorbent could be used many times without decreasing their adsorption capacities significantly. As the results obtained in this study, it was concluded that the new Fe(III)-imprinted thiocyanato-functionalized silica gel sorbent was promising for the selective removal of Fe(III) ions from aqueous media.

## ACKNOWLEDGEMENTS

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