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Removal of Cr(III, VI) by quaternary ammonium and quaternary phosphonium ionic liquids functionalized silica materials

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ABSTRACT

A series of silica-based organic–inorganic hybrid materials were prepared by the sol–gel process for Cr(III) and Cr(VI) adsorption. These silica materials generally had high surface areas, good physical–chemical stability and high thermal stability. Trialkylmethylammonium bis 2,4,4-trimethylpentylphosphinate ([A336][C272]) and trihexyl(tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate (Cyphos IL 104) were explored as porogens to prepare porous silica and as extractants to extract chromium ions. Cyphos IL 104 and [A336][C272] functionalized silica sorbents (SG-2, SG-5) can be effectively used for the removal of Cr(III) and Cr(VI) from aqueous solutions by adjusting pH values, whereas trialkylmethylammonium chloride (Aliquat 336) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) functionalized silica sorbents (SG-3, SG-4) can only be used for the removal of the single chromium species, Cr(VI) or Cr(III). The maximum adsorption amounts of Cr(III) and Cr(VI) were 2.14 and 19.31 mg g^{-1} for SG-2 and 2.32 and 15.29 mg g^{-1} for SG-5. Langmuir and Freundlich isotherm models were used to evaluate the adsorption of Cr(III) and Cr(VI) on sol–gel sorbents. The adsorption kinetics of Cr(III) and Cr(VI) on SG-2 and SG-5 could be well described by pseudo-second-order kinetic model. In terms of Cr(III) and Cr(VI) uptake capacities and kinetics, SG-2 and SG-5 appeared to be more suitable for Cr(III) and Cr(VI) removal than SG-3 and SG-4.

1. Introduction

Heavy metal pollution of soil and groundwater is one of the most significant environmental problems today [1,2]. Chromium compounds are widely used in electroplating, metal finishing, leather tanning industry, and pigment production [3]. Chromium exists in two common oxidation states, Cr(III) and Cr(VI). Cr(VI) is more toxic [4] because of its ability to oxidize other species and its adverse impact on lung, liver and kidney [5]. Cr(III) is much less mobile and less toxic than Cr(VI) and is mainly found bound to organic matter in soil and aquatic environments [6,7].

Various adsorbents have been studied for chromium removal from aqueous solutions, including ion exchanger [8,9], activated carbon [10], activated alumina [11], silica gel [12,13] and biomass [1,14]. Chemically modified silica gel is an attractive sorbent for the extraction and separation of metal ions and various types of compounds, because the silica support does not swell or shrink as polymer resins and unmodified natural materials do [15]. Moreover, the modified silica has a good thermal stability and high metal removal efficiency [16].

Ionic liquids (ILs) are generally considered as environmental benign solvents mainly due to their high thermal stability, very low flammability and negligible vapor pressure [17–20]. As a new type of solvent, template and a diffusion medium for extractant, ILs could be doped into the silica gel matrix and retain their chemical activity [21]. In most papers, Aliquat 336 (trialkylmethylammonium chloride), a mixture of octyl and capryl chains with octyl predominating, is frequently used as a phase transfer catalyst and metal extraction reagent [22–26]. Aliquat 336 showed good characteristics in the removal of trivalent and hexavalent chromium ions from aqueous solutions in their anionic forms such as $Cr(OH)_4^-$, CrO_4^{2-} [27]. The removal and recovery of Cr(VI) from aqueous solutions have been reported from our laboratory using the polymer resins supported ILs with methylimidazolium chloride or sulfate functional groups [28]. Both resins have high adsorption capacities for Cr(VI) in a wide pH range of 1.0–12.0. So far, there are no reports about the use of other ILs in chromium treatment.

In this study, we have synthesized trihexyl(tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate (Cyphos IL 104) and trialkylmethylammonium bis 2,4,4-trimethylpentylphosphinate ([A336][C272]) functionalized silica sorbents (SG-2,

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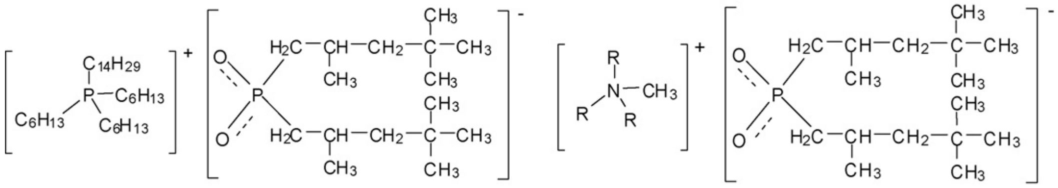
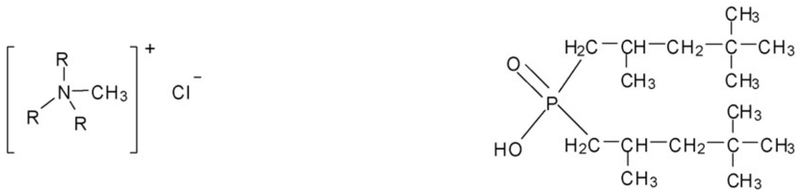


trihexyl(tetradecyl)phosphonium bis
2,4,4-trimethylpentylphosphinate
(Cyphos IL104)

R=Octyl/ capryl
trialkylmethylammonium bis
2,4,4-trimethylpentylphosphinate
([A336][C272])



R=Octyl/ capryl
trialkylmethylammonium chloride
(Aliquat 336)

bis(2,4,4-trimethylpentyl)phosphinic acid
(Cyanex 272)

Fig. 1. Chemical structures of extractants used in this study.

SG-5) by sol–gel process. The adsorption capacities of Cr(III) and Cr(VI) on SG-2 and SG-5 are compared with blank sorbent (SG-1), Aliquat 336 modified silica (SG-3) and Cyanex 272 modified silica (SG-4) to clarify the possible adsorption mechanism.

2. Experimental

2.1. Instrumentation

N_2 adsorption isotherms were recorded through the use of an ASAP-2020 adsorption instrument (Micromeritics, Norcross, GA, USA). Surface areas were calculated using the BET (Brunauer–Emmett–Teller) equation. Pore sizes and pore volumes were obtained by applying the BJH (Barret–Joyner–Halenda) method. TGA data were recorded with Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE, USA). Measurements were conducted by heating the sample from 25 to 800 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere. UV–vis spectra were measured with UVmini-1240 spectrophotometer (Shimadzu, Tokyo, Japan).

2.2. Materials and reagents

Cyphos IL 104 (>95%) and Cyanex 272 (>85%) were kindly supplied by the Cytec Canada Inc. Aliquat 336 (>99%) was purchased from Aldrich. [A336][C272] was synthesized in our laboratory [29]. The chemical structures of extractants are shown in Fig. 1. Stock solutions of Cr(VI) and Cr(III) were prepared by dissolving $K_2Cr_2O_7$ (PT, Tianjin Benchmark Chemical Reagent Co., Ltd., China) and $Cr_2(SO_4)_3{\cdot}6H_2O$ (AR, China National Medicines Co., Ltd., China) in deionized water. The pH of each solution was adjusted with sodium hydroxide and/or hydrochloric acid. Deionized water was used in the preparation of solutions and sol–gel reactions. All other chemicals used were of analytical grade (China National Medicines Co., Ltd., China).

2.3. Preparation of sol–gel sorbents

In a 100 mL beaker, 25 mL of tetraethoxysilane (TEOS) and 2.5 mL of formic acid (0.05 mol L^{-1}) were mixed with deionized water (10 mL) under mild magnetic stirring at room temperature for 6 h. Then 0.004 mol of Cyphos IL 104, Aliquat 336, Cyanex 272 or [A336][C272] was added to the mixture, the gelation occurred within 2 min, 2 min, 28 h or 10 h, separately. The resultant solid materials were dried in vacuum at 40 °C for 24 h. Sol–gel sorbents in this study are referred to as SG-2, SG-3, SG-4 and SG-5, respectively. The blank silica (SG-1) without any extractant was also prepared as described above. The 0.075–0.150 mm particle size fraction was used in our experiments.

2.4. Adsorption and desorption experiments

0.040 g of each sol–gel sorbent was placed in a 50-mL Erlenmeyer flask and treated with 10 mL of Cr(VI) or Cr(III) solutions. The flasks were incubated for 4 h in a rotary shaker at 25 ± 1 °C. Solution samples were then centrifuged for 5 min, and the concentration of chromium was determined spectrophotometrically by diphenylcarbazide (DPC) method. Suitable amount of Cr(VI) solution was diluted to 50 mL with deionized water, then 0.5 mL of H_2SO_4 (1:1, v/v), 0.5 mL of H_3PO_4 (1:1, v/v) and 2 mL of DPC (0.2%) were added to the volumetric flask. The absorbance of this solution was measured at 540 nm after 10 min using a UV–vis spectrophotometer. To analyze Cr(III) concentration, Cr(III) was first converted into the hexavalent state by boiling with potassium permanganate (0.5 mL, 40 g L^{-1}) under acidic conditions. After cooling down to room temperature, 1 mL of 200 g L^{-1} urea was added to the solution and then titrated with 20 g L^{-1} $NaNO_2$ until the solution was colorless. The mixture was diluted to 50 mL with deionized water and 2 mL of DPC (0.2%) was added to the volumetric flask. Thereafter, the Cr(III) concentration was measured at 540 nm after 10 min using a UV–vis spectrophotometer.

The amount of Cr(III, VI) absorbed by the sorbents was determined by the difference. The adsorption efficiency (E) was determined by the following formula:

$$E\,(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

where C_o and C_e represent the initial and final concentrations (mg L^{-1}) of Cr(III, VI) in aqueous phase, respectively. The amount of Cr(III, VI) adsorbed at equilibrium, q (mg g^{-1}), which represents the

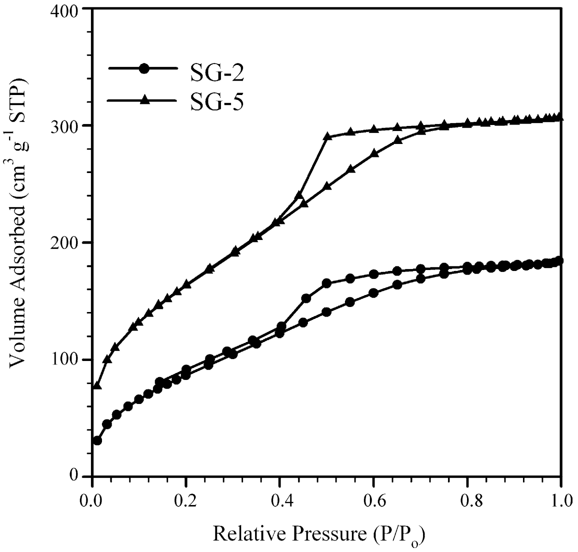


Fig. 2. N_2 adsorption–desorption isotherms for SG-2 and SG-5.

metal uptake, was calculated according to the following equation:

$$q = \frac{(C_o - C_e)V}{M} \tag{2}$$

where V is the volume of metal solution (L) and M is the mass of sorbents (g).

The desorption of Cr(III) and Cr(VI) was carried out using 0.1 mol L^{-1} EDTA, 1.0 mol L^{-1} HCl and 0.1–1.0 mol L^{-1} NaOH solutions. The Cr(III) and Cr(VI) ions loaded sol–gel sorbents were placed in the desorption medium and stirred for 4 h at 25 ± 1 °C. The final concentration of Cr(III) and Cr(VI) ions in the aqueous phase was determined by using a spectrophotometer as described above. The desorption ratio (%) of Cr(III) and Cr(VI) from the sorbents was calculated from the amount of Cr(III, VI) absorbed on the sol–gel sorbents and the final concentration of Cr(III, VI) in the desorption medium. The desorption ratio (%) of Cr(III) and Cr(VI) from the sorbent was calculated from Eq. (3).

$$\text{desorption ratio} = \frac{\text{amount of Cr desorbed}}{\text{amount of Cr adsorbed}} \times 100 \tag{3}$$

All batch experiments were conducted in duplicate under the same conditions, and the relative error between duplicates was less than 5%. The results were reported as mean values.

3. Results and discussion

3.1. Characterization of sol–gel sorbents

Cyphos IL 104 and [A336][C272] acted as porogens to prepare porous silica and as extractants to remove chromium ions from aqueous solutions. ILs adsorbed on the inner surface of porous silica through coulomb interactions and intermolecular interactions. The nitrogen sorption isotherms of SG-2 and SG-5 (Fig. 2) exhibited the typical IV curve, which reflected the formation of the mesoporous structure. As shown in Table 1, Cyphos IL 104 and [A336][C272] functionalized sol–gel materials were quite porous, which may facilitate the adsorption of chromium ions from aqueous solutions.

The thermal stability of SG-2 and SG-5 was investigated by thermogravimetric analysis (TGA) (Fig. 3). The curve of SG-2 showed that degradation process occurred between 271 and 495 °C and the weight loss was 24.1%, due to decomposition of Cyphos IL 104 in the silica. As for SG-5 most of the weight loss occurred between 212 and 500 °C. There were two distinct weight loss stages within this temperature range, 212–353 and 353–500 °C. The first weight loss stage (about 14.2%) was associated with the decomposition of [A336][C272] covered on the silica surface. The second step (about 10.0%) was probably due to the thermal degradation of [A336][C272] within the silica matrix. Thermal decomposition temperature of Cyphos IL 104 and [A336][C272] were 371 °C and 183 °C, respectively. The stability of Cyphos IL 104 doped in SG-2 seemed lower than that of the free Cyphos IL 104. In contrast [A336][C272] doped in SG-5 was more stable than the free [A336][C272].

Table 1
Results of nitrogen sorption experiments of SG-2 and SG-5.

Sorbents	SSA[a] (m^2 g^{-1})	Average pore diameter[b] (Å)	Pore volume (mL g^{-1})
SG-2	343.9	33.2	0.313
SG-5	611.5	32.7	0.509

[a] BET specific surface area.
[b] BJH.

3.2. Effect of pH

The effect of initial pH on the adsorption of Cr(VI) using SG-2, SG-3, SG-4 and SG-5 was studied under the initial metal concentration of 60 mg g^{-1}. As shown in Fig. 4a, the adsorption efficiencies of Cr(VI) on SG-2, SG-3 and SG-5 decreased with increasing pH until the plateau was reached. The optimal adsorption efficiencies of Cr(VI) were observed for the pH range 0–2.0 for SG-2 and SG-5. This is likely due to the fact that Cyphos IL 104 and [A336][C272] are effective extractants of H_2CrO_4, which is the predominant chromium species at pH <2.0 [30,31]. The optimum pH range of Cr(VI) adsorption for SG-3 was 0–5.2, more broad than that of SG-2 and SG-5. The decrease in adsorption efficiency above pH 5.2 was related to the speciation of Cr(VI) and especially to a decrease in the fractions of $HCrO_4^-$ and $Cr_2O_7^{2-}$ with increasing pH [32]. Cyanex 272 is a widely used metal extractant, which is the protonated form of Cyphos IL 104 and [A336][C272] anion. The adsorption of Cr(VI) on SG-4 was occurred at pH <2.0 (Fig. 4a). This was consistent with the result reported by Lanagan and Ibana who observed that significant extraction of Cr(VI) did not occur at pH greater than 2.0 because H_2CrO_4 only existed in the pH range −1.0 to 2.0 [33,34].

The study of adsorption of Cr(III) on SG-2, SG-4 and SG-5 was conducted at pH range of 0–6.0 and initial Cr(III) concentration of 60 mg g^{-1}. In contrast to the adsorption of Cr(VI), the adsorption of

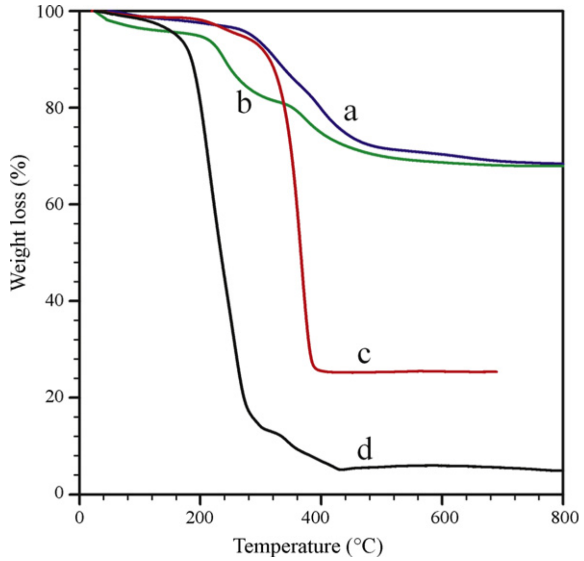


Fig. 3. TGA curves of (a) SG-2, (b) SG-5, (c) Cyphos IL 104 and (d) [A336][C272].

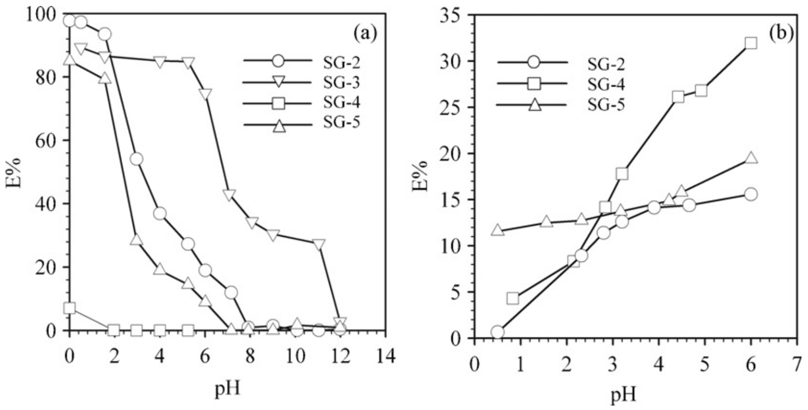


Fig. 4. Effect of initial pH on the adsorption of (a) Cr(VI) (initial concentration, 60 mg L^{-1}) and (b) Cr(III) (initial concentration, 60 mg L^{-1}) on SG-2, SG-3, SG-4 and SG-5 (contact time, 4 h; solid/liquid ratio, 4.0 g L^{-1}).

Cr(III) by SG-2, SG-4 and SG-5 increased dramatically with increasing pH and reached maximum at pH 6.0 (Fig. 4b). It is well known that Cr^{3+} cations in water can undergo hydrolysis and/or complexation reactions, the extent of which depends primarily on the total Cr(III) concentration, on the pH, and on the type of anions present in solutions. The simple hydrolysis of Cr^{3+} can be written as follows:

$$Cr^{3+} + H_2O \rightleftharpoons Cr(OH)^{2+} + H^+ \tag{4}$$

Yun et al. showed that Cr^{3+} and $Cr(OH)^{2+}$ were major species at pH values lower than 5.0, whereby $Cr(OH)^{2+}$ was found to be negligible [35]. The adsorption of Cr(III) by sol–gel sorbents was mainly due to the complexation of Cr(III) species with Cyphos IL 104, Cyanex 272, [A336][C272] doped in SG-2, SG-4, SG-5, respectively. The optimum pH for Cr(III) adsorption on SG-2 and SG-5 was in the range of 4.0–6.0. The high removal efficiency of Cr(III) from solution at pH >6.0 was mainly due to the precipitation of chromium hydroxide ($Cr(OH)_3$). The adsorption of Cr(III) on SG-3 was not investigated in our study. As reported by previous studies, the extraction of Cr(III) by Aliquat 336 was usually investigated in the alkaline solutions [36,37]. $Cr(OH)_4{}^-$ became dominant in solutions at pH exceeding 12.0 and anionic complexes formed in the organic phase containing ammonium cations and $Cr(OH)_4{}^-$ [25]. The difference in the adsorption behavior of Cr(III) and Cr(VI) species on the sorbents could be interpreted by different extraction mechanisms between Cr(VI) and Cr(III).

3.3. Kinetics study

The kinetics of Cr(VI) adsorption on the different adsorbents was further investigated with 60 mg L^{-1} of Cr(VI) solutions in 1.0 mol L^{-1} HCl. The results were plotted as amount adsorbed (mg g^{-1}) versus time (min) (Fig. 5a). It was observed that the adsorption of Cr(VI) on SG-2, SG-3 and SG-5 was rapid from the beginning of the experiment and thereafter it proceeded at a slower rate. Adsorption equilibrium of Cr(VI) on SG-2, SG-5 and SG-3 achieved after 1, 1, and 3 h, respectively. There was almost no adsorption beyond the above time after the maximum adsorption taking place. Adsorption of Cr(VI) by SG-3 occurred slower than that by SG-2 or SG-5 due to their different adsorption mechanisms. The anion of Aliquat 336 ([A336]Cl) transferred to the aqueous solutions with anion-exchange mechanism, but both the cations and anions of Cyphos IL 104 and [A336][C272] still remained in the silica matrix after adsorption.

The uptake kinetics of Cr(III) adsorption to SG-2, SG-4 and SG-5 was studied at pH 4.6 and initial Cr(III) 60 mg L^{-1}. As shown in Fig. 5b, the adsorption for all sorbents occurred primarily within 80 min and then the equilibrium was achieved.

To examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, pseudo-first-order and pseudo-second-order kinetic equations were used to test the experimental data. This pseudo-first-order kinetic model known as the Lagergren equation [38]:

$$\ln\left(1 - \frac{q_t}{q_1}\right) = -k_1 t \tag{5}$$

where q_1 and q_t denote the amounts of adsorption at equilibrium and at time t (mg g^{-1}), and k_1 is the rate constant of first-order sorption (min^{-1}). The pseudo-second-order kinetic model [39]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_2}^2} + \frac{t}{q_2} \tag{6}$$

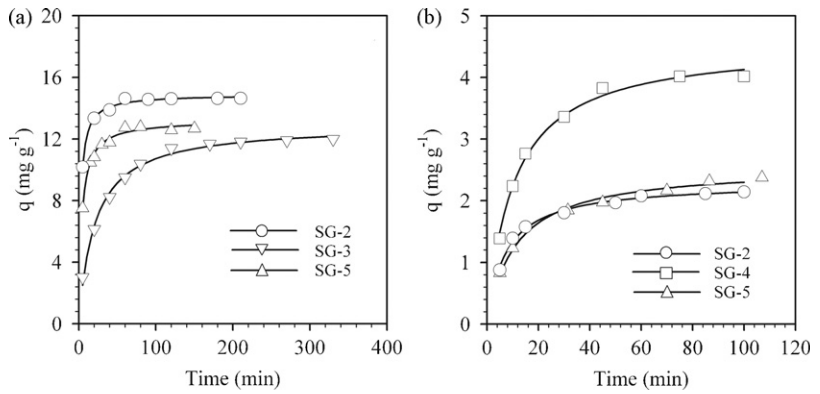


Fig. 5. The kinetic data for (a) Cr(VI) (60 mg L^{-1} Cr(VI) in 1.0 mol L^{-1} HCl; solid/liquid ratio, 4.0 g L^{-1}) and (b) Cr(III) (60 mg L^{-1} Cr(III); pH, 4.6; solid/liquid ratio, 4.0 g L^{-1}) adsorption on SG-2, SG-3, SG-4 and SG-5.

Table 2
The pseudo-first-order and pseudo-second-order kinetics constants for the removal of Cr(III) and Cr(VI) by SG-2, SG-3, SG-4 and SG-5.

Species	Sorbent type	Experimental	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		q_{exp} (mg g^{-1})	R^2	q_1 (mg g^{-1})	k_1 (min^{-1})	R^2	q_2 (mg g^{-1})	k_2 (g mg^{-1} min^{-1})
Cr(III)[a]	SG-2	2.14	0.962	2.05	0.104	0.991	2.29	0.060
	SG-4	4.02	0.988	3.95	0.080	0.993	4.55	0.021
	SG-5	2.38	0.944	2.21	0.076	0.991	2.56	0.035
Cr(VI)[b]	SG-2	14.63	0.917	14.35	0.243	0.992	14.89	0.029
	SG-3	12.00	0.968	11.68	0.033	0.992	12.94	0.004
	SG-5	12.75	0.870	12.33	0.155	0.990	13.22	0.019

[a] Solution pH 4.6, solid/liquid ratio = 4.0 g L^{-1}; initial Cr(III) concentration = 60 mg L^{-1}.
[b] Solution contained 1.0 mol L^{-1} HCl, solid/liquid ratio = 4.0 g L^{-1}, initial Cr(VI) concentration = 60 mg L^{-1}.

where q_2 is the amount of adsorption at equilibrium (mg g^{-1}) and k_2 is the pseudo-second-order rate constant of sorption (g mg^{-1} min^{-1}). The pseudo-first-order and pseudo-second-order kinetics constants for the adsorption of Cr(III) and Cr(VI) on SG-2, SG-3, SG-4 and SG-5 are tabulated in Table 2. The correlation coefficients obtained for the pseudo-second-order kinetic model were equal or greater than 0.990 for all sorbents. The theoretical q_2 values of the pseudo-second-order kinetic model for sorbents were close to the experimental values than those of the pseudo-first-order kinetic model. Therefore, the adsorption kinetics followed the pseudo-second-order kinetic model, suggesting a chemisorption process.

3.4. *Isotherm analysis*

Langmuir and Freundlich isotherm models were used to evaluate the adsorption of Cr(III) and Cr (VI) on sol–gel sorbents. Langmuir is the frequently used single-component adsorption model [40], shown below:

$$q = \frac{bq_{\text{m}}C_{\text{e}}}{1 + bC_{\text{e}}} \tag{7}$$

where q_{m} is the maximum adsorption capacity (mg g^{-1}) and b is a constant related to the adsorption energy (L mg^{-1}).

The Freundlich expression is an equation based on heterogeneous surfaces suggesting that binding sites are not equivalent and/or independent. The Freundlich model is described by Eq. (8) [41]

$$q = KC_{\text{e}}^{1/n} \tag{8}$$

where K and n are the Freundlich constants. K and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The sorption parameters of Langmuir and Freundlich isotherms models, obtained by non-linear regression analysis, together with the correlation coefficients (R^2) are summarized in Table 3. The equilibrium data of adsorption of Cr(VI) and Cr(III) by SG-2, SG-3, SG-4 and SG-5 have been shown as points in Fig. 6. The maximum amounts of Cr(VI) adsorbed were 19.31, 11.05 and 15.29 mg g^{-1}, respectively, for SG-2, SG-3 and SG-5. It is clear from Fig. 6a that the Langmuir model could fit all the experimental data well for Cr(VI) adsorption, as R^2 values are higher than Freundlich model. The Langmuir model served to estimate the maximum adsorption capacities (q_{m}) where they could not be reached in the experiments. The q_{m} values of Cr(VI) adsorbed on SG-2, SG-3 and SG-5 were 19.16, 12.21 and 15.49 mg g^{-1}, respectively. The results were generally in good agreement with the experimental data. The isotherm simulations from Langmuir and Freundlich isotherms for Cr(III) adsorption are shown in Fig. 6b. Freundlich provided a satisfactory fit with R^2 values ranged from 0.991 to 0.997.

3.5. *Adsorption mechanism*

The maximum adsorption capacity of the blank silica SG-1 was 0.12 mg g^{-1} for Cr(VI) and 0.50 mg g^{-1} for Cr(III). The large difference in adsorption capacity levels between SG-1 and other sorbents clearly indicated that the adsorption of chromium ions by sol–gel sorbents was mainly attributed to the entrapped extractants. H_2CrO_4 is the predominant Cr(VI) species in 1.0 mol L^{-1} HCl. The content of extractant doped in sol–gel sorbents was 0.39, 0.45, 0.45 and 0.39 mmol g^{-1} for SG-2, SG-3, SG-4 and SG-5, respectively. Based on extractant content in the sorbent, the adsorption capacity can be calculated with reference to molar extractant content: the equilibrium adsorption capacity of SG-2, SG-3 and SG-5 was 0.95, 0.47 and 0.75 mol Cr(VI) mol^{-1} extractant. Cyphos IL 104 doped in SG-2 extracted Cr(VI) under the undissociated form (H_2CrO_4) through H-bond coordination and formed the complex with the

Table 3
A comparison of Langmuir and Freundlich constants q_{m} (mg g^{-1}), b (L mg^{-1}), K and n resulting from equilibrium uptake studies of Cr(III) and Cr(VI) by SG-2, SG-3, SG-4 and SG-5.

Models	Sorbent	Cr(III)[a]				Cr(VI)[b]			
		q_{exp}	q_{m}	b	R^2	q_{exp}	q_{m}	b	R^2
Langmuir	SG-2	2.14	2.96	0.045	0.954	19.31	19.16	2.19	0.990
	SG-3					11.05	12.21	0.13	0.992
	SG-4	3.98	5.83	0.045	0.979				
	SG-5	2.32	2.31	1.27	0.940	15.29	15.49	1.13	0.992

Models	Sorbent	Cr(III) [a]			Cr(VI)[b]		
		K	n	R^2	K	n	R^2
Freundlich	SG-2	0.316	2.07	0.991	13.0	10.3	0.852
	SG-3				3.95	4.30	0.877
	SG-4	0.556	1.92	0.997			
	SG-5	1.679	11.8	0.991	8.04	6.46	0.897

[a] Solution pH 4.6, solid/liquid ratio = 4.0 g L^{-1}; contact time = 4 h.
[b] Solution contained 1.0 mol L^{-1} HCl, solid/liquid ratio = 4.0 g L^{-1}; contact time = 4 h.

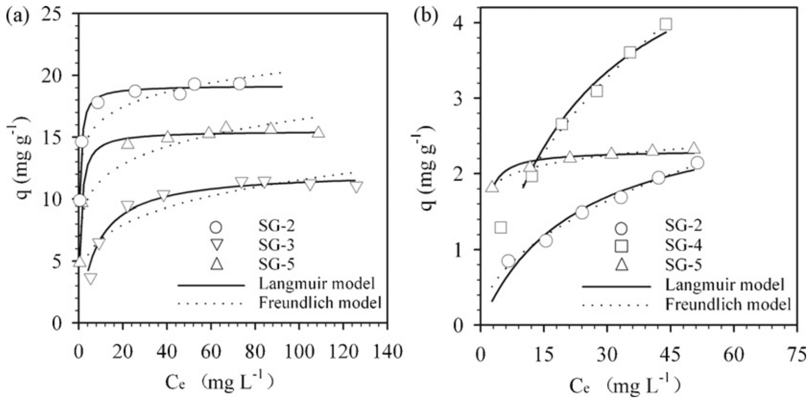


Fig. 6. Adsorption equilibrium isotherms of (a) Cr(VI) (1.0 mol L^{-1} HCl) and (b) Cr(III) (initial pH, 4.6) at 25 °C (solid/liquid ratio, 4.0 g L^{-1}; contact time, 4 h).

ratio of 1:1. An ion association mechanism took place in Cr(VI) uptake in 1.0 mol L^{-1} HCl. Cr(VI) was extracted by Aliquat 336 doped in SG-3 according to an anion-exchange process [42]. As for SG-5, it is difficult to define the appropriate stoichiometric ratio between [A336][C272] and Cr(VI). It seems a complicated mechanism including anion exchange and ion association may play a role in Cr(VI) removal. Cr(III) exists as Cr^{3+}, $Cr(OH)^{2+}$, $Cr(OH)_2{}^{+}$ or a combination of these species in aqueous solutions at pH 4.6 [35,43,44]. Mendoza et al. reported that the stable extracted species $Cr(OH)(HA)_2(NO_3)_2$ and $Cr(OH)A_2$ were formed in nitrate system after 4 h, where HA is Cyanex 272 molecule [45]. We presumed that the adsorption by SG-2 and SG-5 was mainly due to the complexation of Cr(III) species with IL anions.

3.6. Sol–gel sorbents reusability

Sodium hydroxide and hydrochloric acid were carefully chosen as desorbents to recover Cr(III) and Cr(VI) from loaded sol–gel sorbents. Cr(VI) was desorbed from SG-2 and SG-5 by different concentration of NaOH solutions. The data listed in Table 4 indicates that the maximum desorption of Cr(VI) from SG-2 and SG-5 was 99.9% and 99.7% by 1.0 mol L^{-1} NaOH. Compared with 0.1 mol L^{-1} EDTA, 1.0 mol L^{-1} HCl was more suitable for the desorption of Cr(III) from SG-2 and SG-5. Over 90% of Cr(III) was desorbed easily by 1.0 mol L^{-1} HCl. Four cycles of adsorption–desorption experiments were conducted to examine the capability of SG-2 and SG-5 to retain chromium removal capacity using 1.0 mol L^{-1} NaOH and 1.0 mol L^{-1} HCl, separately. After four adsorption–desorption cycles, the adsorption efficiencies of SG-2 and SG-5 decreased 2.8% and 3.6% for Cr(VI), and 8.7% and 7.2% for Cr(III), which was considered as one of direct evidences to evaluate the stability of the sol–gel materials. The main reason might be that the porosity of sol–gel sorbents may facilitate the entrainment loss of extractants. The adsorption capacities of sol–gel sorbents decreased with the loss of extractants content. The results also suggested that NaOH and HCl solutions can be used as desorbents to individually recover the adsorbed Cr(III) and Cr(VI) from SG-2 and SG-5 in the practical industry.

Table 4
Effect of desorbents (10 mL) on the recovery (%) of Cr(III) and Cr(VI) from SG-2 and SG-5 (0.15 g) after adsorption of Cr(III) at pH 4.6 and Cr(VI) at pH 1.7.

Species	Sorbent	Desorbent	Desorption ratio (%)
Cr(VI)	SG-2	0.1 mol L^{-1} NaOH	78.5%
	SG-2	1.0 mol L^{-1} NaOH	99.9%
	SG-5	0.1 mol L^{-1} NaOH	80.2%
	SG-5	1.0 mol L^{-1} NaOH	99.7%
Cr(III)	SG-2	0.1 mol L^{-1} EDTA	70.5%
	SG-2	1.0 mol L^{-1} HCl	90.8%
	SG-5	0.1 mol L^{-1} EDTA	64.2%
	SG-5	1.0 mol L^{-1} HCl	93.1%

4. Conclusions

Quaternary phosphonium and quaternary ammonium ILs functionalized silica (SG-2, SG-5) were prepared by sol–gel process and used as sorbents for the removal of Cr(III) and Cr(VI) from aqueous solutions. The adsorption of both Cr(III) and Cr(VI) on SG-2 and SG-5 could be simply achieved by adjusting pH values. Other sol–gel sorbents doped with Aliquat 336 or Cyanex 272 (SG-3, SG-4) were only suitable for the removal of single chromium species, Cr(III) or Cr(VI), from acidic aqueous solutions. The optimum pH for Cr(III) and Cr(VI) adsorption on SG-2 and SG-5 was in the range of 4.0–6.0 and 0–2.0, respectively. The kinetic data of Cr(III) and Cr(VI) for all sorbents agreed well with the pseudo-second-order equation.

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