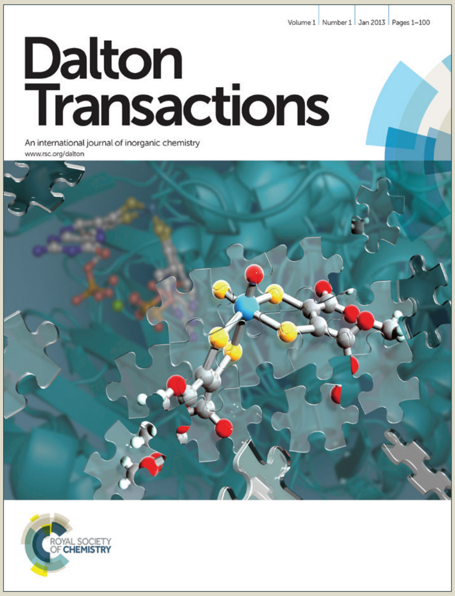
Dalton Transactions

Accepted Manuscript



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Dalton Transactions

An international journal of inorganic chemistry

www.rsc.org/dalton

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Dalton Transactions RSCPublishing

ARTICLE

Facile synthesis of a novel polymeric ionic liquid gel and its excellent performance for hexavalent chromium removal†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th September 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shuojue Wang,[a] Hui-Ling Ma,[a,b] Jing Peng,[a] Youwei Zhang,[a] Jian Chen,[a] Liangliang Wang,[a] Ling Xu,[c] Jiuqiang Li[a] and Maolin Zhai*[a]

A novel polymeric ionic liquid gel (PIL gel) was simply synthesized by γ-radiation-induced polymerization of ionic liquid monomer 1-allyl-3-vinylimidazolium chloride and crosslinking at ambient temperature without any additives. By changing the radiation dose, the properties of the resultant gel including the gel fraction, crosslinking density and equilibrium degree of swelling were optimized. The resultant PIL gel exhibited a superior adsorption ability toward Cr(VI) in aqueous solutions with a broad pH range (1-7) through anion exchange. It was found that the adsorption kinetics followed the pseudo-second-order model. The adsorption of Cr(VI) by the PIL gel obeyed the Langmuir isotherm equation with a theoretical maximum adsorption capacity of 283 mg g^{-1}, twice of the highest value for ionic liquid-based adsorbents that have been reported. In addition, the PIL gel could be recovered using NaCl solution or NaOH solution without much decreasing the adsorption capacity. This work paves the way for scale-up production of PIL gels using radiation technique for potential application in heavy metal removal.

1. Introduction

As a novel class of green solvents, ionic liquids (ILs) have attracted significant attention over the last decade because of their unique properties, such as negligible vapor pressure, excellent thermal and chemical stability, designable structures, high ionic conductivity, and wide electrochemical window.[1, 2] Polymeric ionic liquids (PILs) belong to a subclass of polyelectrolytes, which bear an ionic liquid species in each monomer repeating unit.[3] Combining some of the specific features of ILs with intrinsic properties of polymers, PILs are an emerging research focus in the polymer and materials science due to their particular properties and successful applications in biosensors,[4] catalysis,[5] microwave absorption,[6] and gas separation,[7] etc.

Given the functional groups (i.e. cations such as imidazolium, pyridinium, and pyrrolidinium; anions such as tetrafluoroborate, hexafluorophosphate, and triflate) of PILs, they can be considered as a kind of ion exchangers to remove metal ions from aqueous solution. In fact, ILs[8-11] and supported ILs[12, 13] have been extensively studied in separation processes through ion exchange. However, when ILs are used in separation processes, large amounts of ILs are needed and the recovery of ILs is relatively difficult.[14] Therefore, supported ILs are gradually developed by immobilizing molecules with IL-like structures on inorganic or polymer supports to overcome these shortcomings. Up to now, various kinds of supported ionic liquids have been prepared.[12-14] Unfortunately, the solid supports could hardly provide adsorption sites for metal ions, leading to a limited adsorption capacities of supported ILs. The obstacle would be broken through by direct polymerization of IL monomers. The removal of metal ions by PILs has been reported,[15] but the adsorption capacity is low due to poor affinity of hydrophobic PILs to water. PIL gel based on hydrophilic monomer can overcome the problem. Owing to the three-dimensional networks of PIL gel and the hydrophilic nature of the monomer, PIL gel is insoluble and shows good affinity for water. Despite increased interest in PIL gels during the last few years,[16-19] to the best of our knowledge, there is rarely any published report on this research subject.

PIL gels or gels containing IL-like structures are usually prepared by traditional chemical reactions with the addition of initiators at a relatively high temperature,[16, 20] which are relatively complicated and energy-consuming. A question raised in this paper is: would it be possible to prepare PIL gels without initiators by a simpler and greener procedure? Radiation-induced polymerization and crosslinking is a facile, clean and effective route which utilizes radiation-generated radicals as real initiators. By using this method, hydrogels can be prepared under room temperature in the absence of initiators and catalysts. The technique has been applied in synthesizing hydrogels,[21, 22] but no attempt has been reported on the radiation synthesis of PIL gels.

In this study, a novel PIL gel was easily prepared by gamma irradiation on the neat IL monomer for the first time. Effects of dose on the gel fraction, equilibrium degree of swelling, and morphology of PIL gels were studied. The PIL gel was further used in adsorption of Cr(VI), a widespread and toxic pollutant

Dalton Transactions Accepted Manuscript

in industrial effluents.[23] The adsorption behavior of Cr(VI) was systematically investigated by changing the contact time, solution pH, Cr(VI) concentration and ionic strength. Finally, desorption and recyclability of the adsorbent were also evaluated.

2. Experimental

2.1 Materials

1-allyl-3-vinylimidazolium chloride (AVImCl, ＞99%) was purchased from Lanzhou Greenchem ILS, LICP. CAS. China. Potassium dichromate ($K_2Cr_2O_7$, ⩾99.8%) was obtained from Sinopharm Chemical Reagent Co., Ltd. Other chemicals were analytical-grade reagents and were used as received without further purification.

2.2 Preparation and characterization of PIL gel

2.2.1 Preparation of PIL gel

AVImCl was poured into a glass tube and bubbled with argon for 20 min. Finally, the tube was sealed and subjected to gamma ray irradiation using a ^{60}Co source at the Department of Applied Chemistry of Peking University. All the experiments were conducted at room temperature. After a certain period time of irradiation, the product was then carefully removed from the tube, cut into small pieces and dried in a vacuum oven until constant weight.

2.2.2 Gel fraction and equilibrium degree of swelling (*EDS*)

The sol part of PIL gel was extracted by deionized water and then dried in vacuum to constant weight. PIL gel after removing the sol was used in the following experiments. The dried PIL gel was immersed into deionized water or solutions with various pH, which were adjusted by HCl and NaOH. After 48 h the fully swollen gel was taken out and weighted.

Gel fraction and *EDS* of the PIL gel were defined as

$$\text{Gel fraction (\%)} = \frac{W_g}{W_i} \times 100 \tag{1}$$

$$EDS = \frac{W_e}{W_g} \tag{2}$$

where W_i is the initial weight of a PIL gel, and W_g is the weight of dried sample after extraction; W_e is the weight of fully swollen PIL gel.

2.2.3 Morphology observation and EDX analysis

The fully swollen gel was immersed into liquid nitrogen and then freeze-dried in vacuum until all water was sublimed. The cross-sectional morphology and elemental composition of PIL gel were observed by scanning electron microscopy (Hitachi S-4800, Japan) and energy dispersive X-ray analysis (EDAX Apollo XP, USA), respectively.

2.2.4 Micro-FTIR analysis

Micro-FTIR analysis of PIL gels before and after adsorption was performed on a Nicolet (NICOLET iN10 MX) spectrometer. The spectra were measured in the absorbance mode in the range of 4000-600 cm^{-1}.

2.2.5 XPS analysis

XPS analysis was performed with an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low energy electron flooding for charge compensation. To compensate for surface charges effects, all binding energies (BE) were calibrated using C 1s hydrocarbon peak at a BE of 284.80 eV.

2.3 Adsorption of Cr(VI) onto PIL gel

All adsorption experiments were carried out by using samples containing 20 mg of PIL gel and 25 mL of Cr(VI) solution in a flask. The flasks were placed on a shaker at 160 rpm under 25 ^{o}C. For kinetics experiments, at a specified time interval, the supernatant solution was analyzed for the residual Cr(VI) concentration. In the pH test, the initial pH of Cr(VI) solution was adjusted from 1 to 10 using 1 mol L^{-1} HCl and NaOH. In the isotherm experiment, Cr(VI) adsorption was carried out in Cr(VI) solution with various initial concentrations. The influence of NaCl on the adsorption of Cr(VI) was studied by adding different amounts of NaCl into the solutions. To explore the competitive effect of various coexisting ions on the removal of Cr(VI), flasks containing PIL gel, 140 mg L^{-1} (2.69 mmol L^{-1}) of Cr(VI) and various components ($CaCl_2$, $NiCl_2$, $ZnCl_2$, $NaNO_3$, $Cu(NO_3)_2$, $Mg(NO_3)_2$) in two concentrations (2.69 and 5.38 mmol L^{-1}) were shaken. The concentration of Cr(VI) was measured by UV-Visible Spectrophotometer (UV-3010, HITACHI) at 540 nm.[24] The adsorption of Cr(III) was performed as an comparison with an initial pH of 3.5 and Cr(III) concentration of 155 mg L^{-1}. The concentration of Cr(III) was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES, Leeman, USA). Chromium uptake (q) was calculated as

$$q = \frac{(C_0 - C_e) \times V}{m} \tag{3}$$

The adsorption efficiency (E) was determined as

$$E(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{4}$$

where C_0 and C_e are the concentrations of Cr(VI) or Cr(III) before and after adsorption, respectively; V is the volume of the Cr(VI) or Cr(III) solution and m is the weight of dry PIL gel.

2.4 Regeneration and reusability of PIL gels

Desorption of Cr(VI) was studied as follows: after PIL gel fully adsorbed Cr(VI) ions, 25 mL of NaOH or NaCl solution (1 mol L^{-1}) was added, followed by 12 h shaking at 25 ^{o}C. Distilled water was also used to study desorption behavior of the gels for comparison. The desorption ratio was measured by the following equation:

$$\text{Desorption ratio (\%)} = \frac{m_d}{m_a} \times 100 \tag{5}$$

where m_a is the mass of Cr(VI) adsorbed in the gels and m_d is the mass of Cr(VI) desorbed into the solutions.

The adsorption was also carried out in six consecutive cycles. In each cycle, 25 mL of 140 mg L^{-1} Cr(VI) solution (initial pH = 4.6) was absorbed by 20 mg PIL gel for 12 h. Then the PIL gel was separated from Cr(VI) solution, followed by desorption by NaOH or NaCl solution as described above. After each cycle, the PIL gel was washed with distilled water and used for adsorption in the succeeding cycle. All values were measured in duplicate with the uncertainty within 2%.

3. Results and discussion

3.1 Preparation and characterization of PIL gel

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 2015

When the ionizing radiation deposits on a liquid molecule, it is well known that the electron or free radicals are generated. These active species could induce polymerization of the parent molecule containing vinyl and allyl groups. With the continuous irradiation, crosslinking between the polymer chains could further take place and the gels are expected to be formed in an appreciable yield. In the case of neat AVImCl monomer, after γ irradiation for a certain period of time depending on the dose, it is observed that the AVImCl liquid turns into gels, suggesting that radiation-induced polymerization and crosslinking have taken place. Compared with other methods for synthesis of PIL gels,[16, 19] this radiation-induced process is much efficient and clean without adding any initiators and all the chemical reactions occurs at room temperature. Gel fractions and *EDS* of PIL gels as a function of dose are shown in Fig. 1. The gelation starts from the dose of *ca.* 140 kGy. The gel fraction increases with an increase in the dose. In contrast, *EDS* of PIL gels sharply declines with the increasing dose and then levels off, which is an indication of relatively higher crosslinking density at higher dose and will be discussed later. Similar observation has been reported elsewhere.[25] It is worth to note that the swollen PIL gels synthesized below 180 kGy are very brittle due to high swelling ratios. In this case, it is difficult to measure the accurate weights. All the results indicate that PIL gels with higher crosslinking density are formed at higher dose. As PIL gel formed at 300 kGy has the highest gel fraction together with lowest *EDS*, in the following experiments, PIL gel obtained in this condition was used to avoid the weakening of gel toughness caused by swelling if there is no special indication.[26]

The SEM micrographs of PIL gels synthesized at different doses are given in Fig. 2. It is clear that three-dimensional networks are formed in all PIL gels. The gel at higher dose has smaller pores, indicating a higher crosslinking degree.[27] This is consistent with the *EDS* results. Inside PIL gels with higher crosslinking degree, a restriction in the mobility of the polymer chains results in the decreased water absorption.[28]

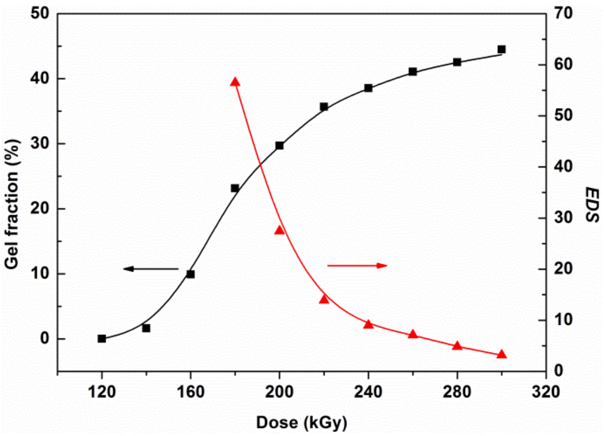


Fig. 1 Gel fractions and *EDS* of PIL gels as a function of dose.

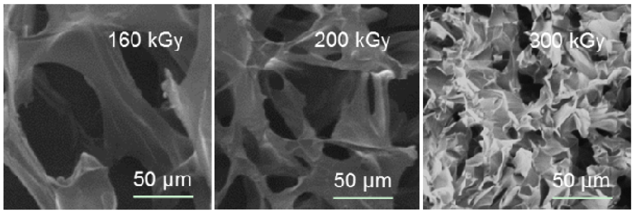


Fig. 2 SEM images of PIL gels prepared at 160, 200 and 300 kGy.

3.2 Adsorption of Cr(VI) onto PIL gels

3.2.1 Adsorption kinetics

Micro-FTIR spectrum of PIL gel after adsorption displays two new adsorption peaks at 938 and 877 cm^{-1} (Fig. S1, ESI†), corresponding to the adsorbed Cr(VI) anions.[29, 30] Adsorption of Cr(VI) onto PIL gel is further confirmed by the appearance of Cr and O signals in the EDX spectrum of PIL gel after contact with Cr(VI) (Fig. S2, ESI†). In order to evaluate the adsorption rate of Cr(VI) onto the resultant PIL gels, the effect of contact time on the Cr(VI) adsorption was studied with an initial Cr(VI) concentration of 140 mg L^{-1} at pH 4.6 ± 0.2. As shown in Fig. 3, there is a burst adsorption step in the initial stage, and almost 90% of the Cr(VI) adsorption is achieved within 90 min. Then the Cr(VI) adsorption rate gradually decreases until equilibrium is reached at about 240 min with a maximum Cr(VI) uptake of *ca.* 177 mg g^{-1}. To ensure complete adsorption of Cr(VI), the contact time was set as 12 h in the subsequent experiments.

Pseudo-first-order and pseudo-second-order kinetic models (expressed as Eqs. (6) and (7), respectively) were used to fit experimental data of Cr(VI) adsorption onto PIL gels.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (6)$$

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

where q_t and q_e (both in mg g^{-1}) are the adsorption capacities at time t (min) and at equilibrium, respectively; k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption process, and k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order model.

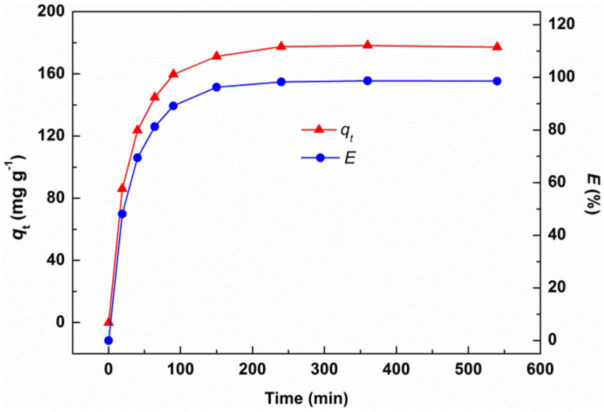


Fig. 3 Cr(VI) uptake as a function of contact time. (pH = 4.6 ± 0.2; [Cr(VI)] = 140 mg L^{-1})

As can be seen from Table 1, high correlation coefficients (>0.99) of the fitting are obtained. However, the correlation coefficient of a pseudo-second-order model (0.999) is slightly higher than that of a pseudo-first-order model (0.994). Furthermore, the estimated q_e from the pseudo-second-order model (184 mg g^{-1}) are closer to the experimental value than that from the pseudo-first-order (151 mg g^{-1}). Therefore, it is suggested that the adsorption kinetics can be described by the pseudo-second-order model, indicating a chemisorption process.[31]

Table 1 The fit results from pseudo-first-order and pseudo-second-order models.

Pseudo-first-order	Pseudo-second-order

Dalton Transactions Accepted Manuscript

k_1 (min^{-1})	q_e (mg g^{-1})	R^2	$k_2\times10^4$ (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
0.0246	151	0.994	3.31	184	0.999

3.2.2 Effect of solution pH

Solution pH is an important factor that will usually affect the surface property of the adsorbent and existing forms of metal ions. The effect of pH on the adsorption of Cr(VI) was studied under an initial Cr(VI) concentration of 140 mg L^{-1}. Fig. 4a displays the dependence of the Cr(VI) adsorption on the solution pH: Cr(VI) removal increases from pH 1 to 2, reaches a plateau and keeps constant at pH 2~6, followed by a steep decline in the alkaline region. As Cr(VI) adsorption capacity remains highest at pH 2~6, the initial pH was selected to be 4.6 in the following experiments.

Cr(VI) exists in various forms such as H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}. Generally, $HCrO_4^-$ is the dominant form at pH < 6, and $Cr_2O_7^{2-}$ represents a small fraction of Cr(VI) species at pH 2~6. In the alkaline pH, the predominant species is CrO_4^{2-}. With the rise of acidity, H_2CrO_4 is formed.[32-34] The following equations display how PIL gel adsorbs Cr(VI) depending on pH. Im^+ is the symbol for imidazolium cation in the PIL gel.

$$\mathrm{Im^+\,Cl^- + HCrO_4^- \rightleftharpoons Im^+\,HCrO_4^- + Cl^-} \tag{8}$$

$$\mathrm{2Im^+Cl^- + Cr_2O_7^{2-} \rightleftharpoons (Im^+)_2Cr_2O_7^{2-} + 2Cl^-} \tag{9}$$

$$\mathrm{2Im^+Cl^- + CrO_4^{2-} \rightleftharpoons (Im^+)_2CrO_4^{2-} + 2Cl^-} \tag{10}$$

$$\mathrm{Im^+Cl^- + OH^- \rightleftharpoons Im^+OH^- + Cl^-} \tag{11}$$

In the pH range from 2 to 6, Eqs. (8) and (9) take place. The relatively low adsorption efficiency at lower pH could be attributed to the existence of H_2CrO_4, which leads to the decrease in electrostatic interaction between Cr(VI) and PIL gel.[35] At the alkaline pH, the dominating Cr(VI) form, CrO_4^{2-}, takes up two active sites of PIL gel with only one Cr(VI) atom (Eq. (10)).[13] Besides, OH^- competes with Cr(VI) ions to combine with imidazolium cations (Eq. (11)).[36] All these account for the decrease of Cr(VI) adsorption at alkaline condition.

It has to be noted that many adsorbents containing imidazole or amino groups for Cr(VI) removal show relatively high adsorption capacity only in a narrow pH range, beyond which the performance of Cr(VI) removal significantly drops due to deprotonation.[32, 37] Owing to the original N^+ groups instead of NH^+ as a result of protonation, PIL gel maintains a high adsorption capacity in a wide pH range similar to other supported ILs.[13, 38] PIL gel has the ability to adsorb almost 100% of Cr(VI) ions at pH 2~6. Even at pH 10.5, PIL gel can still remove 70% of the initial Cr(VI) with a q_e of 126 mg g^{-1}, which is higher than the maximum adsorption capacity of many adsorbents.[31, 39]

In order to investigate the influence of swelling behavior of PIL gel on Cr(VI) uptake, *EDS* of PIL gel was measured in a series of solutions with different pH. As shown in Fig. 4b, low *EDS* (2.3~2.6) of the PIL gels is observed in the pH range of 1~11. Although the pH range of relatively high *EDS* is in accord with the pH range for the highest Cr(VI) uptake, the slight change in the *EDS* with varying pH proves that the effect of *EDS* on Cr(VI) removal in different pH can be neglected.

3.2.3 Adsorption isotherms

The adsorption capacity of PIL gel towards Cr(VI) as a function of Cr(VI) concentration at the equilibrium state was determined at pH 4.6 ± 0.2. The adsorption capacity of Cr(VI) is enhanced with the increase of Cr(VI) concentration until Cr(VI) adsorption reaches ~280 mg g^{-1} (Fig. 5). The adsorption efficiency versus initial Cr(VI) concentration is shown in Fig. S3, ESI†. With the increasing concentration of Cr(VI) from 140 to 207 mg L^{-1}, the adsorption efficiency remains constant (~99%) and then declines. The PIL gel is able to adsorb > 90% of the Cr(VI) ions at initial Cr(VI) concentration < 250 mg L^{-1}.

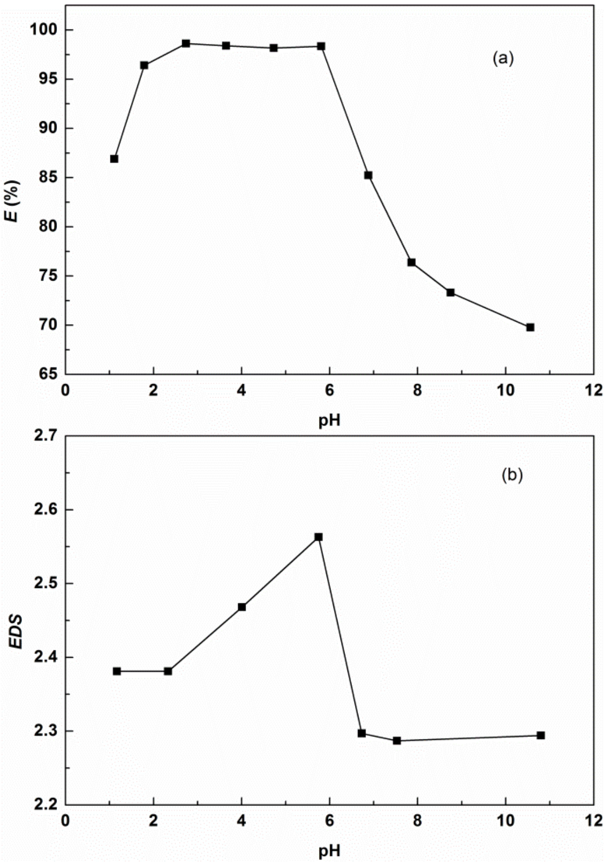


Fig. 4 (a) The effect of solution pH on Cr(VI) adsorption onto PIL gel ([Cr(VI)] = 140 mg L^{-1}); (b) The effect of solution pH on *EDS* of PIL gel.

The obtained data were applied to the Langmuir and Freundlich isotherm models. The Langmuir isotherm is applicable to monolayer adsorption with all adsorption sites identical and energetically equivalent while Freundlich isotherm is employed to describe heterogeneous systems.[29, 40] The Langmuir and Freundlich isotherm models are expressed as Eqs. (12) and (13), respectively.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{12}$$

$$q_e = K_F C_e^{1/n} \tag{13}$$

where q_m (mg g^{-1}) is the maximum adsorption capacity for Cr(VI) and K_L (L mg^{-1}) is the Langmuir constant related to the adsorption energy; K_F and n are Freundlich constants indicating the adsorption capacity and adsorption intensity, respectively.

Langmuir and Freundlich parameters calculated from fitting process, together with the correlation coefficients are listed in Table 2. The linear plot of C_e/q_e versus C_e according to Langmuir isotherm model is also shown in Fig. 5. It is found that the Langmuir isotherm model fits the experimental data much better than Freundlich isotherm model with a much higher correlation coefficient of 0.999, implying homogeneous distribution of adsorption sites and monolayer adsorption.[32] The q_m value is estimated to be 283 mg g^{-1} by the Langmuir model, and is in good agreement with the

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 2015

experimental data. To the best of our knowledge, the theoretical maximum adsorption capacity of supported ionic liquids is found less than 140 mg g^{-1},[38] and the q_m value of the PIL gel is almost twice of that. Because this gel adsorbent is directly from repeat ionic liquid units with intrinsic polymer backbone, the density of the functional groups are high enough to ensure a higher q_m.

A dimensionless separation factor R_L, which is indicative of the feasibility of the adsorption process, can be obtained from the Langmuir adsorption parameter K_L:

$$R_L = \frac{1}{1 + K_L C_0} \tag{14}$$

The R_L values calculated at the tested initial Cr(VI) concentrations in our experiment are all between 0 and 1, implying that PIL gel is a favorable adsorbent for Cr(VI).[41, 42]

The removal of Cr(VI) is not affected by the gels prepared at different dose. PIL gel prepared at 220 kGy, whose *EDS* is 6~7 times of that of PIL gel prepared at 300 kGy, shows a similar adsorption isotherm with a maximum adsorption capacity of 281 mg g^{-1} (Fig. S4, ESI†) because they possess similar densities of adsorption sites (i.e. densities of Cl^- ions). This indicates that the swelling of gel will not affect Cr(VI) adsorption capacity.

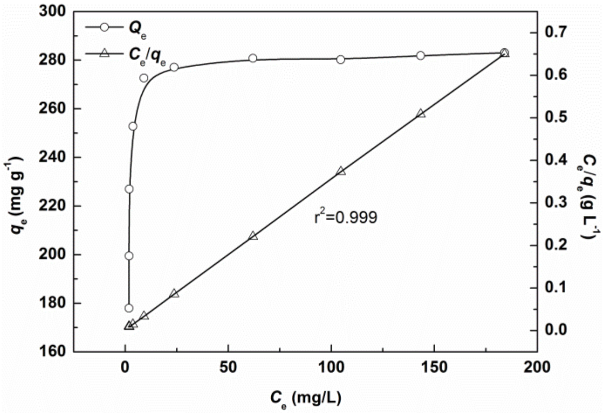


Fig. 5 Experimental Cr(VI) adsorption on PIL gel and Langmuir linear plot. (pH = 4.6 ± 0.2)

Table 2 Isotherm parameters for Cr(VI) adsorption onto PIL gel

Langmuir			Freundlich		
q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F ($mg^{(1-1/n)}$ $L^{1/n}$ g^{-1})	N	R^2
283	1.52	0.999	210	15.3	0.650

3.2.4 Effect of NaCl and other ions on Cr(VI) adsorption

The effect of NaCl on Cr(VI) adsorption was carried out by adding different amounts of NaCl into the initial 140 mg L^{-1} Cr(VI) solution at pH 4.6 ± 0.2. The results are depicted in Fig. 6. It is obvious that Cr(VI) uptake declines with the increasing ionic strength, which can be attributed to the competition for adsorption sites in PIL gel between Cl^- ions and Cr(VI) ions as shown in Eqs. (15) and (16). The addition of NaCl also leads to the restriction of metal ion mobility, which is also responsible for the decrease in Cr(VI) adsorption.[43]

$$Im^+HCrO_4^- + Cl^- \rightleftharpoons Im^+Cl^- + HCrO_4^- \tag{15}$$

$$(Im^+)_2Cr_2O_7^{2-} + 2Cl^- \rightleftharpoons 2Im^+Cl^- + Cr_2O_7^{2-} \tag{16}$$

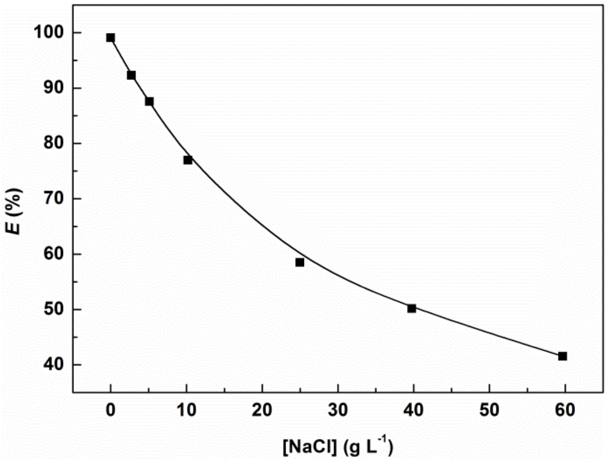


Fig. 6 Effect of NaCl on Cr(VI) adsorption by PIL gel. (pH = 4.6 ± 0.2; [Cr(VI)] = 140 mg L^{-1})

Generally, chrome-plating wastewater contains various kinds of cations and anions such as Na^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cl^-, NO_3^- along with Cr(VI) ions.[44] These ions could interfere in the adsorption of Cr(VI). In order to evaluate the potential of PIL gel for Cr(VI) removal from wastewater, the influence of the coexisting ions on Cr(VI) adsorption was investigated. As shown in Fig. 7, even when the concentrations of $NaNO_3$, $CaCl_2$, $Mg(NO_3)_2$, $Cu(NO_3)_2$, $NiCl_2$, and $ZnCl_2$ are all the double of Cr(VI), almost 88% removal of Cr(VI) can be obtained. The result suggests that PIL gel can effectively adsorb Cr(VI) in the presence of other common ions.

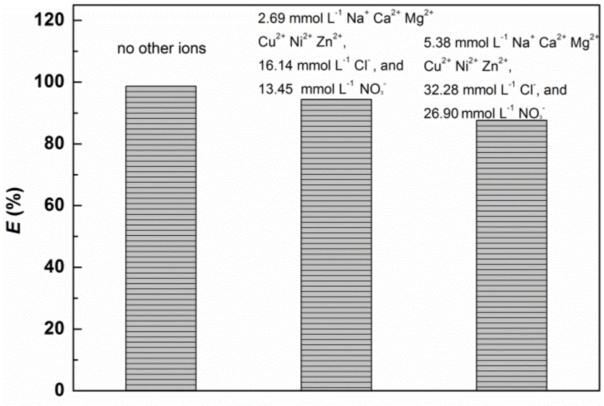


Fig. 7 Adsorption efficiency of Cr(VI) in the presence of other ions (pH = 4.6 ± 0.2; [Cr(VI)] = 140 mg L^{-1}, or 2.69 mmol L^{-1})

3.2.5 Adsorption mechanism

The above results indicate the adsorption process follows an ion exchange mechanism. To further confirm the adsorption mechanism, XPS analysis was performed. The XPS spectra of PIL gel before and after Cr(VI) adsorption are shown in Fig. 8. A small peak corresponding to O 1s signal is observed in the pristine PIL gel, which might be ascribed to a small quantity of water and organics adsorbed on the surface of PIL gel. In the spectrum of PIL gel after adsorption, the intensity of both Cl 2s and Cl 2p peaks remarkably decreases, accompanied by the appearance of Cr 2p signal. Therefore, it is concluded that Cr(VI) ions are adsorbed onto PIL gel through anion exchange. When the negatively charged Cr(VI) ions come into contact with PIL gel with intensive imidazolium cations, they are trapped through electrostatic interaction, take the place of

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 2015

the original counter ion Cl^- and thus tightly adsorbed onto PIL gel. As the imidazolium cations are fixed on the three-dimensional networks of the PIL gel, they are immobile and cannot be exchanged by other cations. For example, PIL gel shows almost no adsorption towards Cr(III). At an initial pH of 3.5 and Cr(III) concentration of 155 mg L^{-1}, the adsorption capacity is lower than 5 mg g^{-1}.

According to the mechanism of anion exchange, the theoretical adsorption capacity at pH 2~6 can be obtained on the assumption that all the Cl^- anions of PIL gel have been exchanged to $HCrO_4^-$ and $Cr_2O_7^{2-}$ (Eqs. (8) and (9)), the two forms of Cr(VI) under the pH condition. The theoretical adsorption capacity is calculated to be 305 mg g^{-1}, which is quite close to q_m (283 mg g^{-1}) from Langmuir isotherm model. This further proves the anion-exchange mechanism and indicates that most active sites of PIL gel are easily accessible.

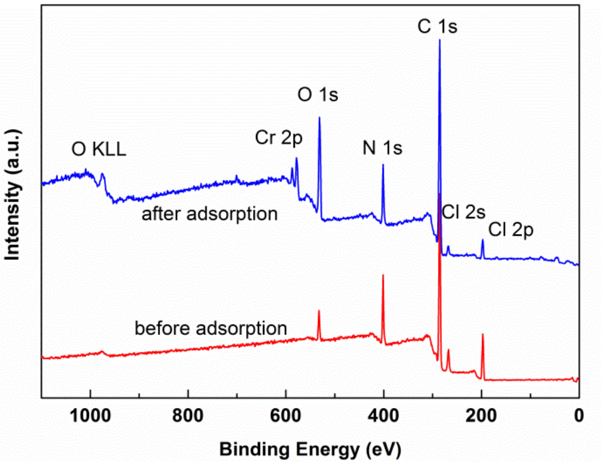


Fig. 8 XPS spectra of PIL gel before and after adsorption.

3.2.6 Regeneration and reusability of PIL gel

The adsorbents for Cr(VI) based on anion exchange mechanism could be generally regenerated by NaCl and NaOH solution.[45, 46] When deionized water was used as desorbing agents for comparison, it is found that only less than 0.1% of Cr(VI) can be desorbed. This suggests Cr(VI) is absorbed into PIL gel by chemisorption via anion exchange instead of physical absorption, which is consistent with the above results. NaCl and NaOH solutions are both capable of desorbing Cr(VI) ions from PIL gel by competing for adsorption sites through anion exchange reactions, with the desorption ratios of ~59% and ~76%, respectively (Fig. S5, ESI†). The desorption ratios are observed at the same level in comparison with other anion exchange resins and can be further improved by using the mixture of NaCl and NaOH.[14]

Reusability of absorbents is important for practical applications. The reusability of PIL gel was investigated by consecutive absorption/desorption cycles. As shown in Fig. 9a, the adsorption capacity of recovered PIL gel by NaCl solution gradually declines with cycling time. This is probably attributed to the occupation of the adsorption sites by the residual Cr(VI) as the desorption ratio is not 100%.[47] After desorption of Cr(VI) by NaOH solution, the PIL gel has an adsorption capacity of 94 mg g^{-1} in the second cycle (Fig. 9b), only 53.4% of the value at the first time. During the re-adsorption process, OH^- ions, which have been absorbed in PIL gel by anion exchange reaction in the desorption procedure, are released to the solution, causing a change in pH from 4.6 to 7.3. Therefore, apart from the occupation of some adsorption sites, the alkaline solution is another reason for the sharp drop in Cr(VI) uptake for the second cycle. Interestingly, the adsorption capacity of PIL gel remains almost constant in the following five cycles when NaOH solution is used to desorb Cr(VI) from PIL gel. Similar phenomenon is observed in the last three cycles using NaCl solution as the adsorption agent. This can be explained by the fact that m_d nearly equals m_a in the last several cycles, resulting in a regenerated PIL gel with almost the same number of active sites as before. After six times, the Cr(VI) uptake of PIL gel is ~69% and 54% of q_e obtained at the first time, but still reach as high as 121 mg g^{-1} (using NaCl solution for desorption) or 94 mg g^{-1} (using NaOH solution for desorption), respectively, which is superior to or nearly equal to the maximum adsorption capacity of many adsorbents.[31, 41, 48, 49] These results indicate that the PIL gel could be used as recyclable absorbent for Cr(VI).

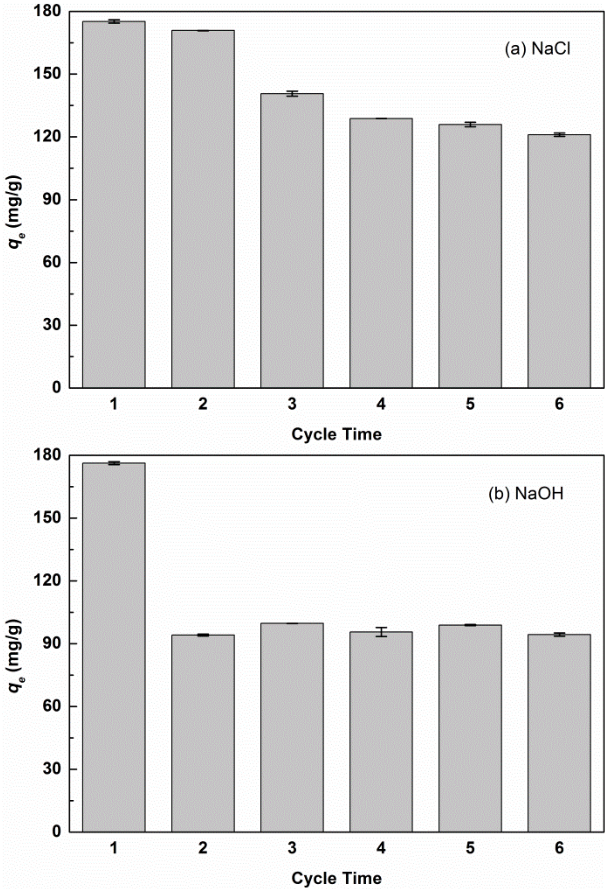


Fig. 9 Effect of cycling time on Cr(VI) adsorption using (a) NaCl solution and (b) NaOH solution to desorb Cr(VI) from PIL gel.

4. Conclusions

By using radiation technique, a novel PIL gel based on AVImCl monomer has been successfully synthesized for the first time. The preparation route is simple and easy to scale up. The resultant PIL gel possesses the advantages of supported ionic liquids in separation of metal ions, including small amounts of ionic liquids used and a high metal ion removal efficiency in a wide pH range. Moreover, compared with supported ionic liquids, the adsorption capacity is remarkably enhanced due to the absence of solid supports and good affinity of PIL gel towards water. Most of the adsorption sites of the PIL gel are easily accessible and the maximum adsorption capacity reaches as high as 283 mg g^{-1} at 25 °C as calculated by Langmuir equation. In addition, the PIL gel can be regenerated and reused for

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 2015

several times with a relatively high removal ability for Cr(VI). Therefore, green separation of metal ions for reducing waste pollution can be expected. This work provides a simple and efficient way to synthesize PIL gels and emphasizes the application of PIL gels for metal ion treatment.

Acknowledgements

The National Natural Science Foundation of China (NNSFC, Project No. 11375019, 21471161) are acknowledged for supporting this research.

Notes and references

[a] *Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory of Fundamental Science, the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
E-mail: mlzhai@pku.edu.cn; Fax/Tel: +86 10 6275 3794
[b] *Beijing Key Laboratory of Radiation Advanced Materials, Beijing Research Center for Radiation Application, Beijing 100015, China*
[c] *Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China*

† Electronic Supplementary Information (ESI) available: Micro-FTIR and EDX spectra of PIL gel before and after adsorption of Cr(VI); effect of initial Cr(VI) concentration on the adsorption efficiency; adsorption isotherm of PIL gel prepared at 220 kGy; desorption ratio after each cycle using NaCl and NaOH solution to desorb Cr(VI) from PIL gel. See DOI: 10.1039/b000000x/

1. M. Gorlov and L. Kloo, *Dalton Trans.*, 2008, 2655-2666.
2. S. J. Wang, J. Z. Liu, L. Y. Yuan, Z. P. Cui, J. Peng, J. Q. Li, M. L. Zhai and W. J. Liu, *Phys. Chem. Chem. Phys.*, 2014, **16**, 18729-18735.
3. J. Y. Yuan and M. Antonietti, *Polymer*, 2011, **52**, 1469-1482.
4. M. S. P. López, D. Mecerreyes, E. López-Cabarcos and B. López-Ruiz, *Biosens. Bioelectron.*, 2006, **21**, 2320-2328.
5. Q. Zhao, P. F. Zhang, M. Antonietti and J. Y. Yuan, *J. Am. Chem. Soc.*, 2012, **134**, 11852-11855.
6. J. B. Tang, M. Radosz and Y. Q. Shen, *Macromolecules*, 2008, **41**, 493-496.
7. J. E. Bara, C. J. Gabriel, E. S. Hatakeyama, T. K. Carlisle, S. Lessmann, R. D. Noble and D. L. Gin, *J. Membrane Sci.*, 2008, **321**, 3-7.
8. Y. Zuo, Y. Liu, J. Chen and D. Q. Li, *Ind. Eng. Chem. Res.*, 2008, **47**, 2349-2355.
9. N. Papaiconomou, S. Genand-Pinaz, J. M. Leveque and S. Guittonneau, *Dalton Trans.*, 2013, **42**, 1979-1982.
10. N. Papaiconomou, G. Vite, N. Goujon, J.-M. Leveque and I. Billard, *Green Chem.*, 2012, **14**, 2050-2056.
11. A. Messadi, A. Mohamadou, S. Boudesocque, L. Dupont and E. Guillon, *Sep. Purif. Technol.*, 2013, **107**, 172-178.
12. B. Lee, H. J. Im, H. Luo, E. W. Hagaman and S. Dai, *Langmuir*, 2005, **21**, 5372-5376.
13. L. L. Zhu, C. Zhang, Y. H. Liu, D. Y. Wang and J. Chen, *J. Mater. Chem.*, 2010, **20**, 1553-1559.
14. L. L. Zhu, Y. H. Liu and J. Chen, *Ind. Eng. Chem. Res.*, 2009, **48**, 3261-3267.
15. H. Mi, Z. G. Jiang and J. Kong, *Polymers*, 2013, **5**, 1203-1214.
16. M. Dobbelin, V. Jovanovski, I. Llarena, L. J. Claros Marfil, G. Cabanero, J. Rodriguez and D. Mecerreyes, *Polym. Chem.*, 2011, **2**, 1275-1278.
17. G. A. Becht, M. Sofos, S. Seifert and M. A. Firestone, *Macromolecules*, 2011, **44**, 1421-1428.
18. X. F. Sui, M. A. Hempenius and G. J. Vancso, *J. Am. Chem. Soc.*, 2012, **134**, 4023-4025.
19. C. Zhang and J. L. Anderson, *J. Chromatogr. A*, 2014, **1344**, 15-22.
20. A. Pourjavadi, M. Doulabi and S. H. Hosseini, *Polymer*, 2012, **53**, 5737-5742.
21. J. Q. Liu, C. F. Chen, C. C. He, J. Zhao, X. J. Yang and H. L. Wang, *ACS Nano*, 2012, **6**, 8194-8202.
22. C. H. Zhu, Y. Lu, J. Peng, J. F. Chen and S. H. Yu, *Adv. Funct. Mater.*, 2012, **22**, 4017-4022.
23. V. Kumari, M. Sasidharan and A. Bhaumik, *Dalton Trans.*, 2015, **44**, 1924-1932.
24. D. Dinda, A. Gupta and S. K. Saha, *J. Mater. Chem. A*, 2013, **1**, 11221-11228.
25. X. M. Zhang, L. Xu, X. Huang, S. C. Wei and M. L. Zhai, *J. Biomed. Mater. Res. A*, 2012, **100A**, 2960-2969.
26. H. Kamata, Y. Akagi, Y. Kayasuga-Kariya, U.-i. Chung and T. Sakai, *Science*, 2014, **343**, 873-875.
27. A. M. Atta, R. A. M. El-Ghazawy, R. K. Farag and A. A. A. Abdel-Azim, *React. Funct. Polym.*, 2006, **66**, 931-943.
28. K. Yokota, A. Abe, S. Hosaka, I. Sakai and H. Saitô, *Macromolecules*, 1978, **11**, 95-100.
29. Y. Koriche, M. Darder, P. Aranda, S. Semsari and E. Ruiz-Hitzky, *Dalton Trans.*, 2014, **43**, 10512-10520.
30. L. F. Zhang, W. Xia, X. Liu and W. Q. Zhang, *J. Mater.Chem. A*, 2015, **3**, 331-340.
31. B. Chen, Z. L. Zhu, J. Hong, Z. P. Wen, J. Ma, Y. L. Qiu and J. H. Chen, *Dalton Trans.*, 2014, **43**, 10767-10777.
32. M. Avila, T. Burks, F. Akhtar, M. Göthelid, P. C. Lansåker, M. S. Toprak, M. Muhammed and A. Uheida, *Chem. Eng. J.*, 2014, **245**, 201-209.
33. C. E. Barrera-Díaz, V. Lugo-Lugo and B. Bilyeu, *J. Hazard. Mater.*, 2012, **223–224**, 1-12.
34. H. Wang, Y. G. Liu, G. M. Zeng, X. J. Hu, X. Hu, T. T. Li, H. Y. Li, Y. Q. Wang and L. H. Jiang, *Carbohyd. Polym.*, 2014, **113**, 166-173.
35. Y. W. Zhang, L. Xu, L. Zhao, J. Peng, C. C. Li, J. Q. Li and M. L. Zhai, *Carbohyd. Polym.*, 2012, **88**, 931-938.
36. J. Y. Qiu, Z. Y. Wang, H. B. Li, L. Xu, J. Peng, M. L. Zhai, C. Yang, J. Q. Li and G. S. Wei, *J. Hazard. Mater.*, 2009, **166**, 270-276.
37. J. N. Li, L. N. Wang, T. Qi, Y. Zhou, C. H. Liu, J. Chu and Y. Zhang, *Micropor. Mesopor. Mater.*, 2008, **110**, 442-450.
38. Y. F. Deng, T. Long, H. Zhao, L. L. Zhu and J. Chen, *Sep. Sci. Technol.*, 2012, **47**, 256-263.
39. J. Fang, Z. Gu, D. Gang, C. Liu, E. S. Ilton and B. Deng, *Environ Sci Technol*, 2007, **41**, 4748-4753.
40. Y. T. Zhou, H. L. Nie, C. Branford-White, Z. Y. He and L. M. Zhu, *J. Colloid Interf. Sci.*, 2009, **330**, 29-37.
41. L. X. Wang, J. C. Li, Q. Jiang and L. J. Zhao, *Dalton Trans.*, 2012, **41**, 4544-4551.
42. L. Y. Yuan, Y. L. Liu, W. Q. Shi, Y. L. Lv, J. H. Lan, Y. L. Zhao and Z. F. Chai, *Dalton Trans.*, 2011, **40**, 7446-7453.
43. A. A. El-Bayaa, N. A. Badawy and E. A. AlKhalik, *J. Hazard. Mater.*, 2009, **170**, 1204-1209.
44. J. Hu, G. H. Chen and I. M. C. Lo, *Water Res.*, 2005, **39**, 4528-4536.
45. A. A. Atia, *J. Hazard. Mater.*, 2006, **137**, 1049-1055.

Dalton Transactions Accepted Manuscript

46. D. M. Chen, W. Li, Y. R. Wu, Q. Zhu, Z. J. Lu and G. X. Du, *Chem. Eng. J.*, 2013, **221**, 8-15.

47. W. T. Yu, L. Y. Zhang, H. Y. Wang and L. Y. Chai, *J. Hazard. Mater.*, 2013, **260**, 789-795.

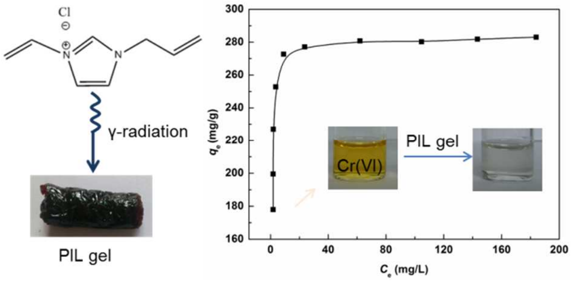
48. T. Karthikeyan, S. Rajgopal and L. R. Miranda, *J. Hazard. Mater.*, 2005, **124**, 192-199.

49. P. A. Terry, *Chemosphere*, 2004, **57**, 541-546.

Dalton Transactions Accepted Manuscript

This journal is © The Royal Society of Chemistry 2015

Graphical abstract



A novel polymeric ionic liquid gel was prepared by gamma radiation at room temperature and showed preeminent adsorption ability toward Cr(VI).

Dalton Transactions Accepted Manuscript