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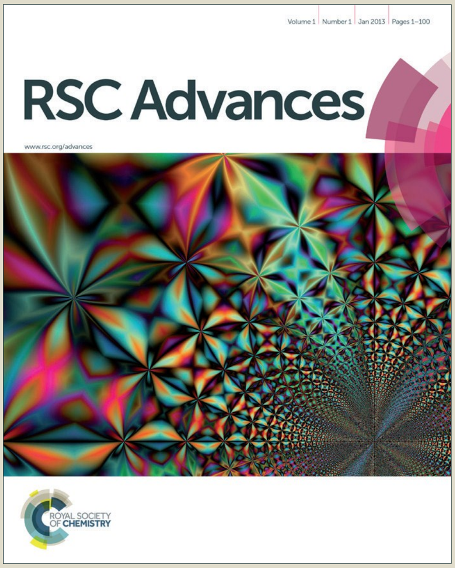

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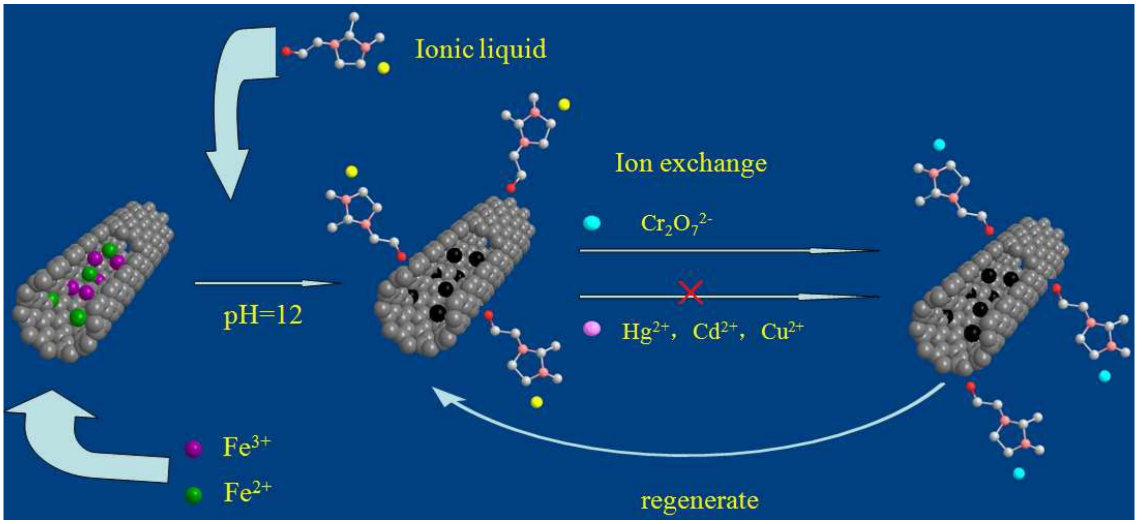

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pH / temperature dependent selective removal of trace Cr(VI) from aqueous solution by imidazolium ionic liquid functionalized magnetic carbon nanotubes

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Carbon nanotubes have excellent adsorption property for metal ions. However, they are lack of selectivity and difficult to separate from solutions. To resolve these problems, magnetic carbon nanotubes were prepared and functionalized with imidazolium ionic liquid in this work. The functionalized magnetic carbon nanotube was used to remove Cr(VI) from water. It was found that the removal was highly selective and sensitive. At acidic conditions, 90% of Cr(VI) could be selectively removed on the ppb level in the coexistence of high concentration of cations like Hg^{2+}, Cd^{2+} and anions such as NO_3^- and SO_4^{2-}. After the adsorption, the material could be collected easily by an external magnet, and then regenerated effectively by using 8% hydrazine hydrate. The high adsorption sensitivity, selectivity and capacity were attributed to the favorable electrostatic attraction, anion exchange affinity and entropy effects. Kinetic analysis indicated that the adsorption process of $Cr_2O_7^{2-}$ was well described by pseudo second order model. The adsorption isothermal analysis revealed that the adsorption process was endothermic, and could be described by Langmuir model. In addition, it is interesting to find that unlike the commonly used absorbents, adsorption capacity of the functionalized material for $Cr_2O_7^{2-}$ increased with increasing temperature.

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Introduction

In recent years, heavy metals contaminations of terrestrial environment have attracted increasing attention due to their highly toxic, persistent, and non-biodegradable properties [1]. Hexavalent chromium is one of the toxic heavy metals, it is highly toxic and can pose significant threat to aquatic life and lead to pollution of public water even if at low levels [2]. According to the regulations of the United States Environmental Protection Agency (USEPA), the permitted concentration of Cr(VI) in drinking water should be less than 0.05 mg L^{-1} [3]. Therefore, the removal of Cr(VI) at low levels from wastewater is of great importance [4].

Adsorption is a promising process for Cr(VI) removal due to its low cost, high efficiency and simple operation [5]. The choice of adsorbent is a key point for adsorption techniques, because adsorption capacity, selectivity, and affinity should be taken into consideration. The traditional adsorbents used for Cr(VI) removal include resins [6], active carbons [7], zeolite [8], nanopartical [9-10], silica gel [11] and among others. Compared with conventional adsorbents, carbon nanotubes (CNTs) have excellent adsorption performance and have been widely used for metal adsorption [12-14] due to their unique structural, physical and chemical properties [15]. However, they have no selectivity for metal ion adsorption, and they are difficult to separate from solutions. To address the separation problem, magnetic carbon nanotubes have been created and utilized for metal ion adsorption [16-18]. This is a great progress although poor selectivity still remains a challenge. Considering the fact that adsorption selectivity of magnetic carbon nanotubes would be improved by their surface functionazation [19], the design and development of new surface functionalized magnetic carbon nanotubes are a new trend in Cr(VI) removal.

Ionic liquids (ILs) are composed of organic cations and inorganic or organic anions, and they have a vanishingly small vapor pressure, making them an attractive alternative to volatile organic solvents [20]. Therefore, ILs have been used as greener solvents for organic synthesis [21], material preparation [22], catalysis [23-24], separation and extraction [25-26]. It has been reported that anionic pollutants have strong affinity with some ILs, and can be extracted by ILs from aqueous solutions [27-29]. However, some disadvantages have weakened their applications, for example, high cost and large amount usage of ILs, dissolution of ILs in aqueous solution which may cause water pollution, and the difficulty in the recovery of ILs. In order to overcome these problems, ILs should be supported on the solid surface. This will reduce the consumption of the ILs, avoid their loss and benefit their recycling [30-33].

In this work, we report a novel material, 1-hydroxyethyl-2,3-methyl imidazolium chloride ionic liquid functionalized magnetic multi-walled carbon nanotube (Fe_3O_4/CNT-IL). This material maintains the advantages of both magnetic carbon nanotubes and ILs. In this way, the disadvantages of carbon nanotubes and ILs can be overcome. The IL functionalized magnetic carbon nanotube has been applied to remove Cr(VI) from aqueous solution. It is found that trace Cr(VI) can be adsorbed by Fe_3O_4/CNT-IL efficiently and selectively due to the strong electrostatic force between anionic $Cr_2O_7^{2-}$ and cationic imidazolium. In deed, 90% of Cr(VI) at 0.028 mg L^{-1} can be removed, and many cations and anions do not interfere the removal. The adsorption capacity of Cr(VI) is controlled by pH value and temperature of the solution. After the adsorption process, the Fe_3O_4/CNT-IL can be separated easily by an external magnet and Cr(VI) adsorbed by the material can be recovered by a reduction agent. The material can be regenerated and reused at least four cycles without decrease of adsorption capacity. The removal process is simple and low cost. These findings indicate that the material may be a promising adsorbent for the removal of Cr(VI) from wastewaters on the ppb level.

Results and discussion

Characteristics of the Fe_3O_4/CNT-IL

XRD patterns of CNT-COOH and Fe_3O_4/CNT-IL were shown in Figure S1. The peaks located at $2\theta=25.927^{\circ}$ and 43.588° were the characteristic peak of CNT. The diffraction peaks of Fe_3O_4 nanoparticles were observed at $2\theta=30.171^{\circ}$, 35.510°, 53.491°, 57.187° and 62.618°. These data are in good agreement with those of Fe_3O_4 nanoparticles (JCPDS No. 19-0629) reported previously [34]. The presence of Fe_3O_4 in the as-prepared material was supported by their indexes diffraction peaks shown in Figure S1.

To confirm the presence of Fe_3O_4 nanoparticals inside MWCNT, the material was characterized by a TEM with an accelerating voltage of 200 kV. For the preparation of TEM specimens, the Fe_3O_4/CNT-IL composite was dissolved in doubly distilled water and dropped onto a carbon coated copper, as shown in Figure S2. It was obviously that a few Fe_3O_4 nanoparticles were located inside the nanotube bundles. Therefore, the material would be stable in acidic solutions and could be separated from aqueous solution conveniently by an external magnet.

In order to confirm that the ionic liquid was really functionalized on the surface of magnetic carbon nanotube, the oxidized carbon nanotube (CNT-COOH), as-prepared magnetic carbon nanotube (Fe_3O_4/CNT-COOH), ionic liquid functionalized magnetic carbon nanotube (Fe_3O_4/CNT-IL) and the pure ionic liquid were analyzed by TGA under the protection of N_2 at a heating rate of 10 $^{\circ}min^{-1}$ from 20 to 800 ℃. The obtained TGA curves (Figure S3) indicated that the ionic liquid was successfully functionalized on the carbon nanotube. It was also found that CNT-COOH had a high thermal stability and showed 16% weight loss during the entire heating cycle, and the magnetic carbon nanotube (Fe_3O_4/CNT-COOH) prepared by loading Fe_3O_4 on the surface of carbon nanotube exhibited only 11% weight loss due to the thermal stability of Fe_3O_4 in N_2 atmosphere. However, the ionic liquid functionalized magnetic carbon nanotube (Fe_3O_4/CNT-IL) exhibited a significant weight loss in the temperature range from 210 ℃ to 280 ℃. Then the weight loss became as slow as CNT-COOH and Fe_3O_4/CNT-COOH, and a weight loss of 28% was finally observed. This is different from pure ionic liquid which had a significant weight loss within the temperature range from 310 ℃ to 370 ℃. In addition, from the weight loss data of Fe_3O_4/CNT-COOH and Fe_3O_4/CNT-IL, it was found that amounts of the ionic liquid on the ionic liquid functionalized magnetic carbon nanotube was about 17%.

The resulting CNT-COOH, Fe_3O_4/CNT-COOH and Fe_3O_4/CNT-IL were also characterized by FT-IR spectroscopy analysis. It can be seen from Figure S4 that CNT-COOH and Fe_3O_4/CNT-COOH exhibited the characteristic bands at 1577.69 cm^{-1} and 1574.95 cm^{-1} resulted from the C=C stretching of main structure of multi-walled carbon nanotube [35], and the adsorption at 3432.67 cm^{-1} and 3401.73 cm^{-1} resulted from the O-H stretching of carboxylic group. In comparison with CNT-COOH and Fe_3O_4/CNT-COOH, some new bands were observed on the Fe_3O_4/CNT-IL samples. The bands at 2854.70 and 2934.77 cm^{-1} were assigned to the stretching of C-H in $–CH_3$ or $–CH_2–$ of the ionic liquid, the bands at 1631.72 cm^{-1} was assigned to the stretching of –C=C– in the imidazolium ring of the ionic liquid, 1108.41 cm^{-1} was assigned to the stretching of C-O in the ester of the material, and the band at 1725.06 cm^{-1} was resulted from the C=O stretching of ester group. These results indicated that ionic liquid was chemically grafted on the surface of the magnetic carbon nanotubes.

Effect of pH on the removal of Cr(VI)

Solution pH value is one of the most important factors influencing the removal process of metal ions. It can affect not only the existing form of chromium, but also the property of adsorbents. The effect of pH value on Cr(VI) removal by CNT, CNT-COOH, Fe_3O_4/CNT-IL and CNT-IL was shown in Figure 1. Obviously, the removal process was highly dependent on pH value of the solutions.

It is known that the materials were protonated under highly acidic conditions, especially at pH < 2.0. In this case, Cr(VI) existed in the negative charged form of $HCrO_4^-$, thus Cr(VI) could be removed by the protonated carbon nanotubes through electrostatic attraction. Moreover, Cr(VI) could be reduced into Cr(III) at pH < 2.0 [36]. This means that part of Cr(VI) may be reduced by CNT to form Cr(III) at pH < 2.0, which also promoted removal of Cr(VI). Consequently, nearly 100% removal percentage was observed, and no difference was found by different adsorbent materials.

However, it was found that at pH=3-8, the removal percentage of Cr(VI) by ionic liquid functionalized carbon nanotubes (Fe_3O_4/CNT-IL and CNT-IL) was 40-60% higher than that by carbon nanotubes (CNT and CNT-COOH). This clearly indicated that the removal efficiency could be improved significantly after the functionalization of ionic liquid on carbon nanotube. It is known that when pH > 2.0, Cr(VI) existed in the form of $Cr_2O_7^{2-}$, the oxidation-reduction reaction could be neglected [36]. To confirm this point, Cr(III) content in the supernatant after 2h adsorption at 65 ℃ was determined by spectrophotometric method [37]. However, no Cr(III) was observed in the supernatant within experimental error. This indicates that Cr(VI) was totally adsorbed but not reduced by Fe_3O_4/CNT-IL, and the removal process was dominated by adsorption. With the increase of solution pH value, the removal percentage of Cr(VI) by carbon nanotubes (CNT and CNT-COOH) decreased rapidly due to the weaker protonation of the materials and the lower positive charge density on these materials. Compared with CNT and CNT-COOH, the ionic liquid functionalized carbon nanotubes (Fe_3O_4/CNT-IL and CNT-IL) have more active sites, which are attributed to the functionalization of imidazolium cations. Thus more Cr(VI) could be adsorbed by these two ionic liquid functionalized materials, and higher removal percentage was observed. It was also indicated that the removal percentage of Cr(VI) by Fe_3O_4/CNT-IL was lower than that by CNT-IL (see Figure 1). The reason is that Fe_3O_4 in Fe_3O_4/CNT-IL has no adsorption for Cr(VI). Although Fe_3O_4/CNT-IL has lower removal efficiency than CNT-IL, the Fe_3O_4/CNT-IL adsorbent material could be separated easily from solutions by an external magnet after the adsorption process. This makes it very simple to recover and reuse the adsorbent.

On the other hand, in the highly basic solutions, especially at pH > 10.0, Cr(VI) existed in the form of CrO_4^{2-}, which has lower affinity for imidazolium cations than $Cr_2O_7^{2-}$. Meanwhile, high concentration of OH^- might interfere with the adsorption of CrO_4^{2-}. Therefore, only 10% of Cr(VI) could be removed under such a pH condition. Overall, in order to remove Cr(VI) efficiently by Fe_3O_4/CNT-IL and to avoid the oxidation of carbon nanotube, pH 3.0 was chosen in the next studies.

Effect of adsorbent dosage on the removal of Cr(VI)

The effect of the amount of Fe_3O_4/CNT-IL on the removal of Cr(VI) was examined by adsorption experiments. For this purpose, 25 mL of solution at pH 3.0, containing 50 μg of Cr(VI) and different amounts of Fe_3O_4/CNT-IL, was shaken for 12 h at 25 ℃. Then the concentration of Cr(VI) in the supernatant was determined by spectrophotometry, and the removal percentage was calculated by Eq. (1).

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (1)$$

In Eq. (1), C_0 and C_e are the concentrations of Cr(VI) before and after adsorption (mg L^{-1}), and R (%) stands for the removal percentage.

As shown in Figure S5, the removal percentage increased with increasing adsorbent dose and remained constant when the adsorbent dose was increased from 20 mg to 50 mg. As the adsorbent dose was higher than 20 mg, almost 100% Cr(VI) could be removed. This could be explained by the fact that at higher adsorbent dose, more chemically active sites were available to interact with Cr(VI).

Adsorption kinetics

Figure 2 represents the effect of contacting time on Cr(VI) removal by Fe_3O_4/CNT-IL. It was found that the removal percentage of Cr(VI) increased with increasing contacting time, and the rate is higher at initial stages. For sorption kinetics, it was observed that about 80% removal percentage was achieved for Cr(VI) within 2 h in the concentration range studied. The initial rapid adsorption may be due to the availability of more chemically active sites. Moreover, imidazolium cations of the ionic liquid grafted on the surface of carbon nanotubes might decrease the mass transfer resistance when Cr(VI) was adsorbed on Fe_3O_4/CNT-IL. Therefore, shorter equilibrium time was observed.

Next, the pseudo first order and pseudo second order models expressed by Eqs. (2) and (3) [38]:

$$\ln\frac{(q_e - q_t)}{q_e} = -k_1 t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad (3)$$

were used to describe the adsorption processes of Cr(VI) by Fe_3O_4/CNT-IL. In Eq. (2), k_1 is the pseudo first order rate constant (min^{-1}) of the adsorption, and q_e and q_t (mg g^{-1}) are the amounts of metal ion adsorbed at equilibrium time t (min), respectively. The values of ln(q_e-q_t) were calculated from the experimental data and used to plot against t (min). In Eq. (3), k_2 is the pseudo second order rate constant of the adsorption. The values of q_e and k_2 could be calculated from slope and intercept of the linear plot of t/q_t vs. t. The kinetic parameters acquired from fitting results were summarized in Table S1.

It can be seen from Table S1 that the pseudo second order model provided better correlation coefficients than the pseudo first order model, and the calculated equilibrium adsorption capacities ($q_{e,cal}$) from the pseudo second order model agreed better with the experimental values. This suggests that the pseudo second order model is more suitable for describing the adsorption kinetics of Cr(VI) by Fe_3O_4/CNT-IL. It was reported that adsorption behavior of the pseudo second order model suggested a chemisorption process [39], and this implied that these adsorbents could be applied to remove low concentration of metal ions [40]. Thus, the adsorbent developed in this work would be a promising candidate to remove low concentration Cr(VI) from wastewater.

Adsorption isotherms

Temperature may greatly influence the property of ionic liquid and the affinity between adsorbent and adsorbate. Figure 3a shows the influence of temperature on Cr(VI) removal by Fe_3O_4/CNT-IL. It was found that the removal process was temperature dependent. At T < 45 ℃, about 80% of Cr(VI) was removed. However, when T > 45 ℃, the removal percentage of Cr(VI) increased rapidly with increasing temperature, and reached 100% at T = 65 ℃. This phenomenon is related to the relative interaction strength of imidazolium cation of the ionic liquid with its Cl^{-1} anion and $Cr_2O_7^{2-}$. For the sake of comparison, we calculated the Coulomb force of imidazolium cation with Cl^{-1} and $Cr_2O_7^{2-}$ approximately from the charge and radius of imidazole, Cl^{-1} and $Cr_2O_7^{2-}$ [41-42], and the result showed that interaction of imidazolium cations with $Cr_2O_7^{2-}$ was stronger than that with Cl^{-1}. At lower temperatures, Cl^- in the ionic liquid could not be exchanged efficiently by $Cr_2O_7^{2-}$ due to its strong electrostatic interaction with imidazolium cations. However, the electrostatic interaction would be decreased with increasing temperature, resulting in the more exchangeable Cl^{-1} and higher removal efficiency of Cr(VI). The adsorption property of Fe_3O_4/CNT-IL is different from the commonly used adsorbent whose adsorption efficiency often decreases with the increase of temperature [43].

In order to further study the influence of temperature on Cr(VI) removal, the effect of temperature on the removal of different concentrations of Cr (VI) was also investigated. The adsorption data were analyzed by using Langmuir and Freundlich adsorption isotherm models, which are applicable to highly heterogeneous surfaces. From the liner form of Langmuir isotherm [44], the equation is given as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (4)$$

where q_e is the equilibrium amount of Cr(VI) adsorbed on the absorbent (mg g^{-1}), q_m is the maximum adsorption capacity of Cr(VI) on the adsorbent (mg g^{-1}), C_e describes the equilibrium concentration of Cr(VI) (mg L^{-1}), and K_L is the Langmuir adsorption constant (L mg^{-1}), which is related to the adsorption energy.

The Freundlich model [44] can be presented by

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (5)$$

where q_e and C_e have the same meanings with those in the Langmuir model, and K_F and n are Freundlich constants related to the maximum adsorption capacity and the adsorption intensity, respectively.

Figure 3b presents the adsorption isotherms of Cr(VI) on the Fe_3O_4/CNT-IL. The calculated Langmuir and Freundlich constants were summarized in Table S2. It can be seen that the Langmuir model exhibited relative higher values of regression coefficients than Freundlich model, and the theoretical values of adsorption capacities obtained from Langmuir model were close to the experimental values. These results indicated that the Langmuir model was more suitable to describe the adsorption isotherms.

Thermodynamic analysis

Thermodynamic analysis of an adsorption process may provide information on its spontaneity and on the stability of the adsorbed phase. The change in the standard Gibbs energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated from the following equations:

$$\Delta G^0 = -RT\ln K_L \qquad (6)$$

$$\ln K_L = -\Delta H^0/RT + \Delta S^0/R \qquad (7)$$

where R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$), T is thermodynamic temperature (K), and K_L is the equilibrium constant obtained from the Langmuir isotherm. It is clearly indicated that values of ΔG^0 could be directly calculated from the equilibrium constants, and those of ΔH^0 and ΔS^0 could be obtained from the slope and intercept of the linear plot of ΔG^0 versus T. The results were given in Table 1.

It is clear that the values of ΔG^0 were negative, indicating favorable adsorption of $Cr_2O_7^{2-}$ on Fe_3O_4/CNT-IL adsorbent. The ΔH^0 and ΔS^0 values of the adsorption reaction are positive, and $T\Delta S^0$ is always greater than ΔH^0 in value. This suggests that the adsorption of $Cr_2O_7^{2-}$ on Fe_3O_4/CNT-IL is controlled by entropy changes [45]. The positive entropy changes for the adsorption can be explained from the fact that $Cr_2O_7^{2-}$ is well solvated in water, in order to adsorb this anion on the surface of Fe_3O_4/CNT-IL, the anion has to lose part of its hydration sheath, leading to an entropy increase. Although hydration of Cl^{-1} released from the ionic liquid in aqueous solution decreases the entropy, the entropy increase resulted from dehydration of $Cr_2O_7^{2-}$ is predominant because of its much bigger volume. This supposition has been verified by the reported hydration entropy data [46]: $\Delta S^0 (Cr_2O_7^{2-}) = 261.9$ J $mol^{-1}K^{-1}$, $\Delta S^0(Cl^{-1}) = 56.5$ J $mol^{-1}K^{-1}$. On the other hand, the observed positive ΔH^0 values suggest endothermic process of adsorption. This may be due to the dehydration of solvated $Cr_2O_7^{2-}$ and the reduction of the electrostatic interaction between imidazolium cation and Cl^{-1}, which are energy required processes.

Generally, the value of ΔG^0 for physical adsorption (-20 to 0 kJ mol^{-1}) is much greater than that for chemical adsorption (-80 to -400 kJ mol^{-1}) [38]. ΔG^0 Value (around -25 kJ mol^{-1}) obtained in this work was between the values for physical adsorption and chemical adsorption, which indicates that adsorption of Cr(VI) by Fe_3O_4/CNT-IL involves both physical and chemical adsorptions.

Removal of trace Cr(VI) from water

In order to test the removal sensitivity by Fe_3O_4/CNT-IL, aqueous solutions of Cr(VI) at the concentrations of 0.028 and 0.085 mg L^{-1} were prepared. 25 mg of Fe_3O_4/CNT-IL was added into a bottle, and then 25 mL of aqueous Cr(VI) solution with a given concentration at pH=3.0 were added. The solution was shaken for 12 h at 25℃, 50℃ and 70℃, respectively, and then the concentration of Cr(VI) in the supernatant was determined by ICP-MS. The experimental results were listed in Table 2.

It was found that ppb level of Cr(VI) could be removed efficiently by Fe_3O_4/CNT-IL. After adsorption, the concentration of Cr(VI) in the solution was lower than the permitted concentration of Cr(VI) in drinking water advised by USEPA (0.05 mg L^{-1}) [3]. It was also observed that the removal percentage was influenced by temperature of the system. The relatively high temperature would be beneficial to the removal of Cr(VI), for example, at 25℃, the removal percentage was 68%, while 21% increase was observed at 70℃ for an aqueous solution containing 0.028 mg L^{-1} of Cr(VI). This is obviously different from the commonly used absorbents, indicating that the ionic liquid functioned material maintains the property of ionic liquid, and the adsorption ability of Fe_3O_4/CNT-IL can be modulated significantly by temperature.

Adsorption selectivity of Cr(VI)

The effects of cations (Hg^{2+}, Cd^{2+} and Cu^{2+}), inorganic anions (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) and organic anions (acetate and citrate) on the removal of Cr(VI) were investigated, and the results were illustrated in Figure 4. It was found from Figure 4a that Hg^{2+}, Cd^{2+} and Cu^{2+} had no influence on $Cr_2O_7^{2-}$ adsorption even when the concentration of interfering cations was 110 times higher than that of $Cr_2O_7^{2-}$. At pH=3.0, cations such as Cd^{2+}, Cu^{2+} and Hg^{2+} were positively charged, they were repelled by the positively charged Fe_3O_4/CNT-IL, thus they did not interfere with $Cr_2O_7^{2-}$ adsorption. By contrast, anionic $Cr_2O_7^{2-}$ could be adsorbed by the positively charged Fe_3O_4/CNT-IL through electrostatic attraction interactions. Consequently, the material can selectively adsorb $Cr_2O_7^{2-}$ from aqueous solutions even at high concentration of coexisting cations.

Inorganic anions such as Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} are common coexisting anions with $Cr_2O_7^{2-}$. The effects of these anions on $Cr_2O_7^{2-}$ adsorption were also investigated. As shown in Figure 4b, these anions did not interfere with $Cr_2O_7^{2-}$ adsorption even if their concentrations were 2500, 2000, 1300 and 1000 times higher than that (0.076 mmol L^{-1}) of $Cr_2O_7^{2-}$, respectively. The effect of anions on

$Cr_2O_7^{2-}$ adsorption followed the order of $Cl^- < NO_3^- < SO_4^{2-} < PO_4^{3-}$, which is consistent with anion exchange affinity order reported in the literature [47]. Obviously, the anion with higher valence, smaller hydrated radius and greater polarizability has stronger competing effect.

The effect of organic anions on $Cr_2O_7^{2-}$ adsorption was presented in Figure 4c. It is clear that these two organic anions did not interfere with $Cr_2O_7^{2-}$ adsorption even if their concentrations were 2500 and 1300 times higher than that (0.076 mmol L^{-1}) of $Cr_2O_7^{2-}$, respectively. In addition, the effect of organic anions was found to follow the order: acetate < citrate. This suggests sthat the anions with higher valence have higher interference.

Based on the above analysis, it is clear that the selectivity of carbon nanotube was greatly improved by the functionalization of ionic liquid, and $Cr_2O_7^{2-}$ could be selectively adsorbed by Fe_3O_4/CNT-IL in the coexistence of cations such as Hg^{2+}, Cd^{2+}, Cu^{2+} and anions such as Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, acetate and citrate.

Regeneration of Fe_3O_4/CNT-IL

After adsorption of Cr(VI), the Fe_3O_4/CNT-IL could be collected easily from aqueous solution by a hand held magnet. The desorption of Cr(VI) and the regeneration of Fe_3O_4/CNT-IL were carried out by using 8% hydrazine hydrate (a reduction reagent), and an average desorption percentage of 80.4% (n=4) was obtained (Figure S6). There are two advantages in the use of this reduction reagent. Firstly, Cr(VI) can be reduced into Cr(III) which is not toxic, and cannot be adsorbed by Fe_3O_4/CNT-IL. Thus the purpose for desorption was achieved. Secondly, the desorption condition is mild compared with the use of high concentration of aqueous NaOH. This is beneficial to the regeneration and recycle of the material. In deed, since the formation of Fe_3O_4 in the inner core of carbon nanotube and the chemical functionalization of the IL on carbon nanotube, Fe_3O_4/CNT-IL shows good stability in the solution. Moreover, sequential adsorption-desorption cycles were carried out four times by using the same adsorbent, no loss of the adsorption capacity was observed.

Comparison with other adsorbents

For comparison, Table 3 shows the removal efficiency of Cr(VI) by other adsorbents reported in the literatures. Considering the adsorption capacity and equilibrium time, the adsorption property of Fe_3O_4/CNT-IL is better than the other materials, except for activated carbon. Although activated carbon exhibited better adsorption capacity and shorter equilibrium time, it was lack of selectivity, and difficult to separate, regenerate and reuse. The cost for preparation of Fe_3O_4/CNT-IL may be higher than that of activated carbon and carbon nanotubes. However, Fe_3O_4/CNT-IL can be easily recovered, regenerated and reused. These results indicate that Fe_3O_4/CNT-IL is an efficient material for Cr(VI) removal from aqueous solution, and this material has higher cost performance.

Experiment section

Chemicals

Multi-walled carbon nanotubes (MWCNTs, purity > 95%) used in the present work were purchased from Nanjing XFNANO Mater. Tech. Co., Ltd. 1-Hydroxyethyl-2,3-methyl imidazolium chlorine ionic liquid was purchased from Lanzhou Institute of Chemical Physics, Chinese Academic of Science. All the other chemicals were commercially available analytical reagents.

Preparation of ionic liquid functionalized magnetic carbon nanotube (Fe_3O_4/CNT-IL)

In order to increase the content of –COOH, multi-walled carbon nanotubes were oxidized under reflux in 65% nitric acid solution for 30 min at 130 ℃. The oxidized multi-walled carbon nanotubes (CNT-COOH) were filtered, washed with deionized water until the filtrate was neutral, and then dried under vacuum for 24 h at 60 ℃.

The following two steps were used to prepare ionic liquid functionalized magnetic multi-walled carbon nanotubes. In the first step, ionic liquid was grafted on the CNT-COOH via esterification reaction. For this purpose, CNT-COOH was added into $SOCl_2$ (30 mL), and the solution was refluxed for 1 h. Excess of $SOCl_2$ was removed by rotary evaporator under reduced pressure, then 30 mL of anhydrous THF was added, followed by the addition of 1.0 g of 1-hydroxyethyl-2,3-methyl imidazolium chlorine ionic liquid. The mixture was stirred for 12 h at room temperature, and the product was collected, and then washed by THF, anhydrous alcohol and deionized water for several times until no absorbance in filtrate was observed. Thereafter, the material was dried under vacuum for 24 h at 60 ℃. In the second step, ionic liquid functionalized carbon nanotube was magnetized using a procedure adapted from Goh et al [54]. In brief, 2.98 g of $FeCl_3\cdot 6H_2O$ and 1.53 g of $FeSO_4\cdot 7H_2O$ were dissolved in 100 mL of deionized water, and then 1.0 g of the CNT-IL was added into the solution. The mixture was sonicated for 1 h and the air in the inner core of multi-walled carbon nanotubes was extracted by a vacuum pump to facilitate the uptake of the iron solution into the carbon nanotubes. The solution was stirred vigorously for 12 h at 70 ℃ under N_2 condition, and the pH value was adjusted to 11-13 using ammonium hydroxide. The system was kept refluxed at the boiling point of the solution for 2 h. Finally, the ionic liquid functionalized magnetic carbon nanotube was collected by an external magnet. To clean the surface of the Fe_3O_4/CNT-IL, the material was washed with dilute hydrochloric acid and deionized water, then washed with anhydrous alcohol for several times, and dried under vacuum for 24 h at 60 ℃.

Characterization and Analysis

CNT-COOH and Fe_3O_4/CNT-IL were analyzed by X-ray diffraction (XRD), and the patterns were recorded in the 2θ range of 10 - 80° with a scan rate of 0.02°/0.4s using a D8-AXS diffractometer (Bruker, Germany) equipped with a Cu K_α radiation (λ=0.15406Å). Fe_3O_4/CNT-IL samples were examined by transmission electron microscopy (TEM) using a JEM 2100 microscope (JEOL, Japan). The thermogravimetric analysis (TGA) curves of the prepared samples were obtained using a NETZSCH-Gerätebau thermogravimetric analyzer (GmbH, Germany) under nitrogen atmosphere. The organic groups on the surface of the multi-walled carbon nanotubes were examined by FT-IR spectroscopy (Bio-Rad, America). ELAN DRC-e inductively coupled plasma mass spectrometer (Perkin Elmer, USA) and TU-1810 UV-Vis spectrophotometer (Persee General Instrument Co., Ltd., China) were used for the determination of metal ion concentrations.

Adsorption Experiments

All the Cr(VI) adsorption experiments were conducted in a glass vessel, into which a certain amount of Fe_3O_4/CNT-IL and aqueous Cr(VI) were added. The initial pH value of the aqueous solution was adjusted by 0.5 mol L^{-1} of HCl or 0.05 mol L^{-1} of NaOH with negligible volume. After the pH value was adjusted to 1.8 - 10.0, the solution was shaken by a water bath shaker. Then the adsorbent was collected by a hand held magnet, and the concentration of Cr(VI) in the supernatants was determined by 1,5-diphenyl carbazide spectrophotometric method with a determination limit of 0.004 mg L^{-1}. For low concentration samples, Cr(VI) was determined by inductively coupled plasma mass spectrometry (ICP-MS) with a detection limit of

0.001 mg L^{-1}. The adsorption capacity and removal percentage of Cr(VI) were calculated by equations (8) and (1):

$$q_e = \frac{(C_0 - C_e)V}{\text{m}} \qquad (8)$$

In Eq. (8), q_e represents the equilibrium adsorption capacity (mg g^{-1}), C_0 and C_e are the concentrations of Cr(VI) before and after adsorption (mg L^{-1}), m is the mass of the adsorbent (mg), and *V* is the volume of aqueous Cr(VI) solution (mL).

Conclusions

In this work, the introduction of imidazolium ionic liquid to the surface of magnetic carbon nanotube can significantly increase the adsorption selectivity, sensitivity and capacity of Cr(VI). The material maintains the characteristics of ionic liquid, carbon nanotube and magnetic material such as high selective, high surface area, easy separation and recycling. The as-prepared material has been applied to remove Cr(VI) from aqueous solutions and the process was highly depending on pH value and temperature of the solution. The adsorbent has the following advantages: i) the significantly reduced consumption of ionic liquid, the cost of the removal process, and the loss of ionic liquid into water; ii) the lowered mass transfer resistance and the shorten equilibrium time for the adsorption; iii) the improved dispersibility in water and excellent separation performance from aqueous solutions; iv) high adsorption sensitivity, selectivity and adsorption capacity, concentration of Cr(VI) as low as 0.028 mg L^{-1} can be removed efficiently in the coexistence of Hg^{2+}, Cd^{2+}, Cu^{2+}, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, acetate and citrate; v) the material can be easily regenerated and recycled.

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Notes and references

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†Electronic Supplementary Information (ESI) available: [Kinetic parameters for the pseudo first order and pseudo second order model for Cr(VI) adsorption onto Fe_3O_4/CNT-IL(Table S1). Langmuir and Freundlich parameters for Cr(VI) adsorption on Fe_3O_4/CNT-IL(Table S2). XRD patterns of (a) CNT-COOH and (b) Fe_3O_4/CNT-IL (Figure S1). The TEM images of Fe_3O_4/CNT-IL(Figure S2). The TGA curve of (a) CNT-COOH, (b) Fe_3O_4/CNT-COOH, (c) Fe_3O_4/CNT-IL and (d) ionic liquid under the protection of N_2(Figure S3). FT-IR spectrum of (a) CNT-COOH, (b) Fe_3O_4/CNT-COOH and (c) Fe_3O_4/CNT-IL (Figure S4). Effect of adsorbent dosage on Cr(VI) removal by Fe_3O_4/CNT-IL (Figure S5). Adsorption-desorption cycle of Fe_3O_4/CNT-IL for Cr(VI) (Figure S6)].

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Figure captions

Figure 1. The influence of pH value on Cr(VI) removal by different materials

Figure 2. Effect of contacting time on the removal of Cr(VI) by Fe_3O_4/CNT-IL

Figure 3. (a) Effect of temperature on Cr(VI) removal by Fe_3O_4/CNT-IL; (b) Adsorption isotherm of Cr(VI) by Fe_3O_4/CNT-IL

Figure 4. Effects of coexisting inorganic cations, inorganic anions and organic anions on Cr(VI) removal

Scheme 1. Preparation of ionic liquid functionalized magnetic multi-walled carbon nanotube

Table 1. Thermodynamic parameters for Cr(VI) adsorption on Fe_3O_4/CNT-IL at pH 3.0

T(K)	$10^{-3}K_L$(L mol^{-1})	ΔG^0(kJ mol^{-1})	ΔH^0(kJ mol^{-1})	ΔS^0(J mol^{-1} K^{-1})
298	2.60	-19.5	61.4	273
313	15.08	-25.0		
328	25.48	-27.7		

Table 2. Removal of Cr(VI) on the ppb level by Fe_3O_4/CNT-IL at different temperatures (n=3)

Temperature /℃	Concentration of Cr(VI) /mg L^{-1}		Total Cr removal percentage %
	Before adsorption	After adsorption	
25	0.028	0.009	68
50	0.028	0.007	75
70	0.028	0.003	89
25	0.085	0.018	79
50	0.085	0.013	85
70	0.085	0.007	92

Table 3. The equilibrium time for the removal of Cr(VI) using different adsorbents

Adsorbent	dosage of adsorbent	Concentration of Cr(VI) (mg L^{-1})	Equilibrium time (h)	Adsorption amount q_m (mg g^{-1})	Reference
oxidized multi walled carbon nanotubes	0.1mg/mL	6	65	4.26	[48]
activated carbon	1mg/mL	44	10	90.99	[49]
activated carbon	0.8mg/mL	50	48	23.5	[50]
activated carbon coated with quaternized poly (4-vinylpyridine)	1mg/mL	226	24	53.7	[51]
multi-walled carbon nanotubes	10mg/mL	0.1	12	—	[52]
Ce^{3+} doped $ZnFe_2O_4$	0.5mg/mL	60	72	57.24	[53]
Fe_3O_4/CNT-IL	1mg/mL	80	12	55.43	This work

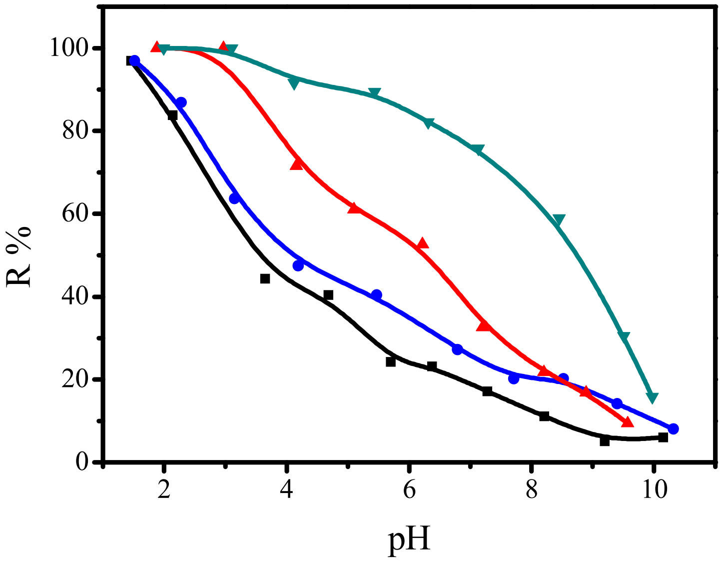


Figure 1. The influence of pH value on Cr(VI) removal by different materials: ■, CNT; ●, CNT-COOH; ▲, Fe_3O_4/CNT-IL; ▼, CNT-IL; adsorbent dosage, 25mg; $C_{[Cr(VI)]} = 2.0$ mg L^{-1}; temperature, 25 ℃; and contacting time,12 h.

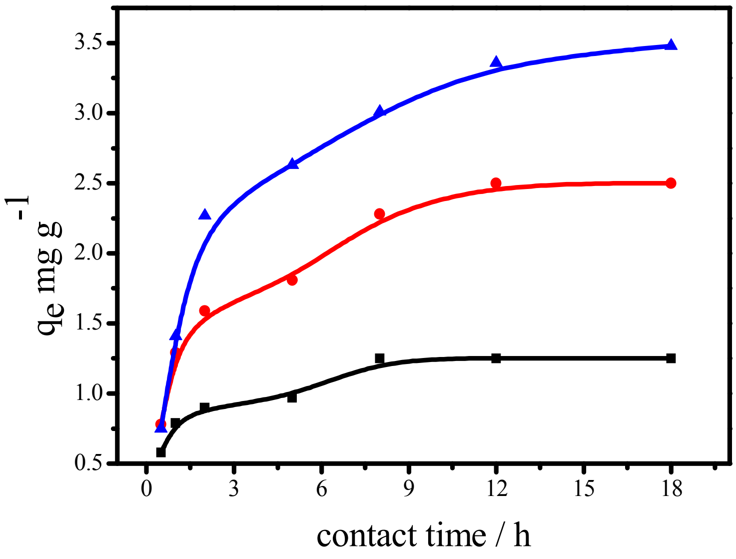


Figure 2. Effect of contacting time on the removal of Cr(VI) by Fe_3O_4/CNT-IL. ■, $C_{[Cr(VI)]}$=1 mg L^{-1}; ●, $C_{[Cr(VI)]}$=2 mg L^{-1}; ▲, $C_{[Cr(VI)]}$=3 mg L^{-1}; adsorbent dosage, 25mg; pH=3.00 ± 0.05, temperature, 25 ℃.

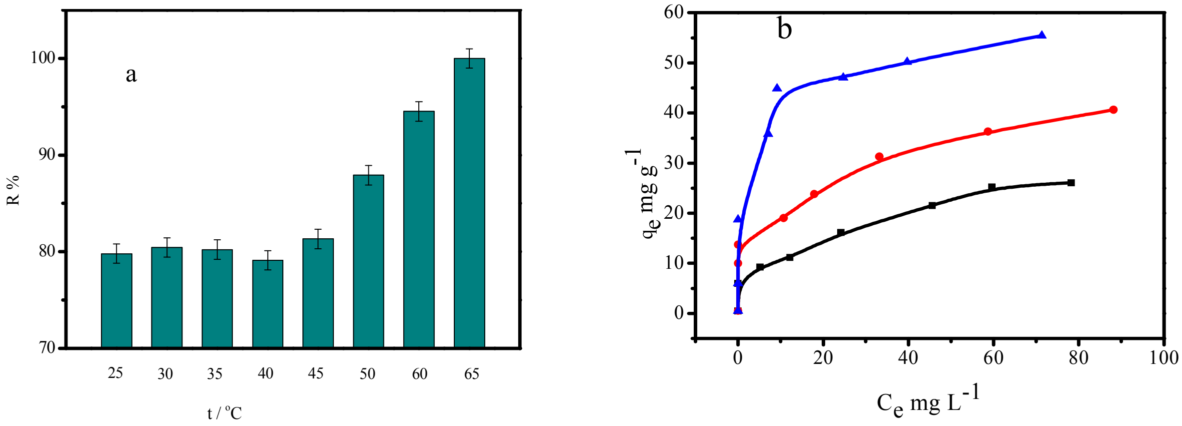


Figure 3. (a) Effect of temperature on Cr(VI) removal by Fe_3O_4/CNT-IL: adsorbent dosage, 25mg; pH=3.00 ± 0.05, $C_{[Cr(VI)]}$ = 2.0 mg L^{-1}, contacting time, 2 h; (b) Adsorption isotherm of Cr(VI) by Fe_3O_4/CNT-IL: ■, 25 ℃; ●, 40 ℃; ▲, 55 ℃; adsorbent dosage, 25mg; pH=3.00 ± 0.05; contacting time,12 h.

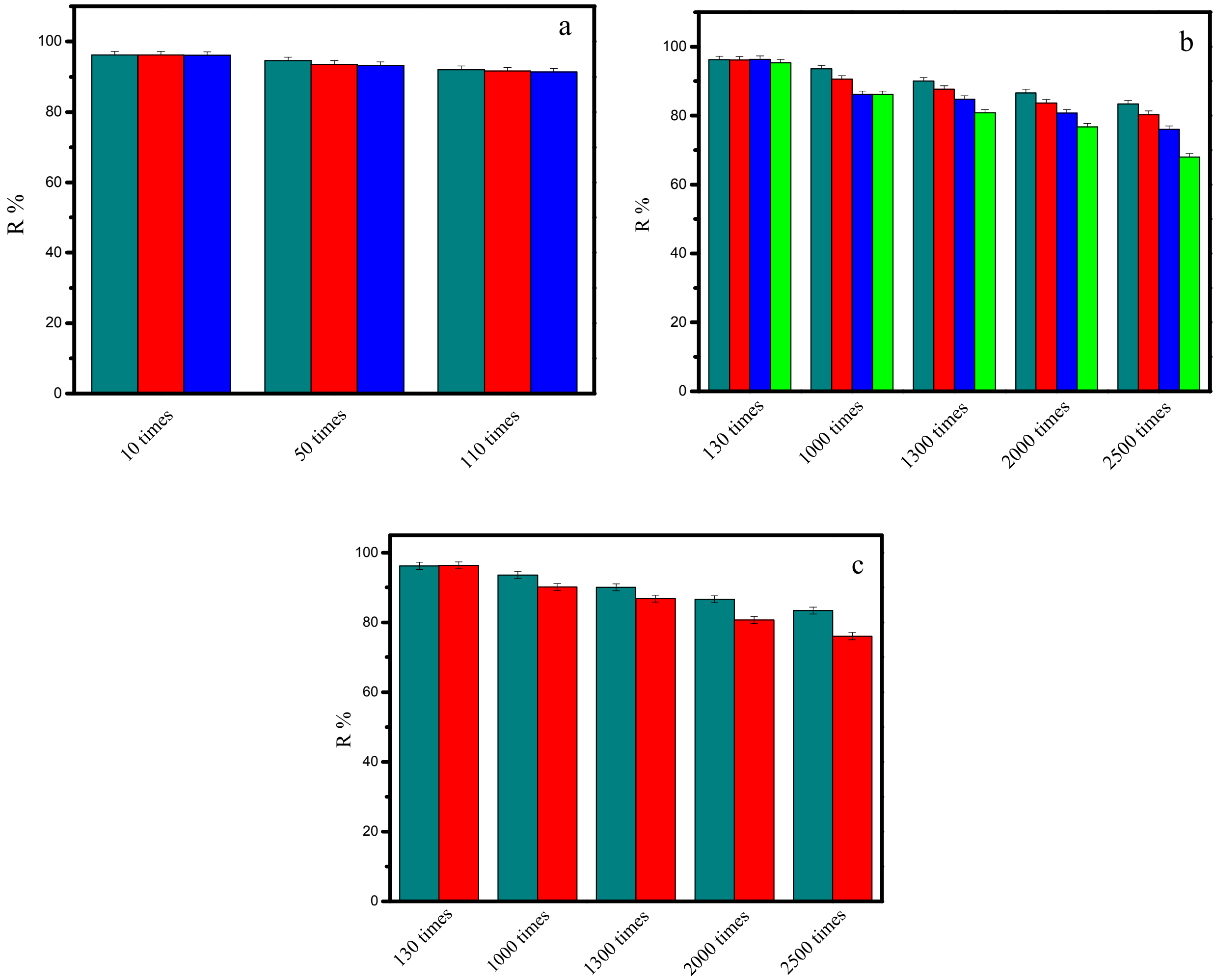
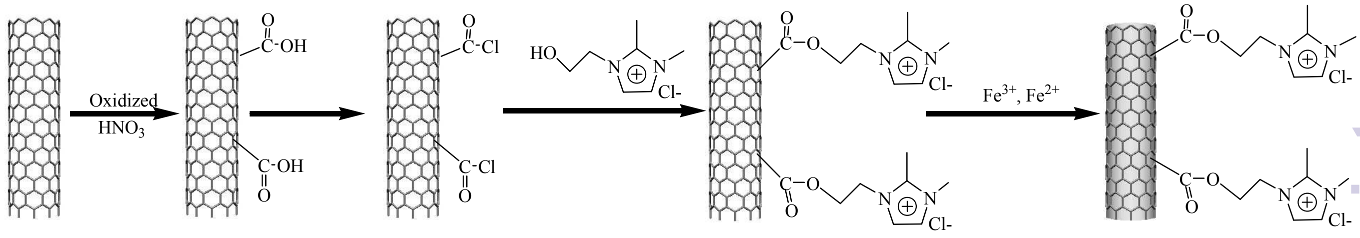


Figure 4. Effects of coexisting inorganic cations, inorganic anions and organic anions on Cr(VI) removal: (a) ■, Hg^{2+}; 🟥, Cd^{2+}; 🟦, Cu^{2+}; (b) ■, Cl^{-1}; 🟥, NO_3^-; 🟦, SO_4^{2-}; 🟩, PO_4^{3-}; (c) ■, acetate; 🟥, citrate; adsorbent dosage, 25 mg; pH=3.00 ± 0.05, $C_{[Cr(VI)]}$ =0.076 mmol L^{-1}, temperature, 55℃, contacting time, 3 h.



Scheme 1. Preparation of ionic liquid functionalized magnetic multi-walled carbon nanotube.