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Adsorption behaviour of functional grafting particles based on polyethyleneimine for chromate anions

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ABSTRACT

Polyethyleneimine (PEI) was first grafted on the surfaces of micro-sized silica gel particles in the manner of the coupling graft, forming the grafting particles PEI/SiO_2. Afterward, for the grafted PEI, two polymer reactions, tertiary amination reaction and quaterisation, were allowed to be carried out in turn, and a kind of functional composite particles, QPEI/SiO_2, was obtained. QPEI/SiO_2 particles were used as solid adsorbent in the removal of chromate anions from aqueous solution. The static adsorption experiments (batch method) were performed, the effects of various factors on the adsorption capacity of QPEI/SiO_2 were examined, and the dynamic desorption experiments were also carried out. The experimental results show that QPEI/SiO_2 particles have strong adsorption ability for CrO_4^{2-} ions by right of electrostatic interaction, and the saturated adsorption amount actually reach up to 0.14 g/g. The isothermal adsorption behaviour is fitted to Langmuir model. The adsorption ability of QPEI/SiO_2 particles for CrO_4^{2-} ions is affected greatly by the quaterisation degree of the grafted PEI macromolecules. The QPEI/SiO_2 particles with higher quaterisation degrees have greater adsorption capacities. The adsorption ability of QPEI/SiO_2 particles for CrO_4^{2-} ions is nearly independent of pH values of the medium. QPEI/SiO_2 particles have excellent eluting and regenerating property as a mixed solution of NaOH and NaCl is used as eluent.

1. Introduction

The contamination caused by heavy metals is a serious environmental problem because of their toxicity to many life forms. Among various heavy metals, chromium poses severe threats to public health. Chromate as a species of hexavalent chromium is known to be high toxic and have powerful carcinogenic effect [1–5], and the maximum permissible level of chromate salt in drinking and industrial wastewater were set by the Environmental Protection Agency (EPA) to be 50 and 200 μg/L, respectively [6]. The chromium pollution mainly results from the wastewater and wastes discharged by leather tanning, electroplating, metallurgy, chemical engineering, mining industries, and so on. Chromate anion is readily transported in ground water and causes the contamination of drinking water because it is highly water-soluble and mobile. In the face of the seriousness of chromium contaminations, efforts have been devoted to treating chromate-contaminated water with several methods, such as adsorption, chemical reduction, ion exchange, membrane-based separation and biological treatment [7–13]. Among these methods, the adsorption technique is better effective and simply, and have widely been studied in the past decades. Except to anion exchange resins [14,12], clay minerals (for example bentonite) and zeolite often are used as solid adsorbent for the removal of chromate from wastewater because of their high specific area and low cost. However, the surface of these materials is usually charged negatively, so the adsorption and elimination effect for the chromate anions is poorer. Therefore, the researchers modify these clay minerals with cationic surfactants, and utilize the cationic characteristics of these surface-modified materials to enhance the removal efficiency for chromate anions [15–19].

Are there more effective solid adsorbents for the removal of chromate? It can be expected that the solid adsorbents with high performance can be prepared by grafting functional polymers onto the surfaces of inorganic micro-particles. The resulted composite materials can combine well the functionality of the functional polymers and the many excellent properties of inorganic micro-particles, such as high specific area, strong mechanical property, fine chemical and thermal stability and low cost.

Polyethyleneimine (PEI) is a kind of water-soluble polyamine, and there is a mass of nitrogen atoms of amine groups on its macromolecular chains. The commercial PEI always is a branched macromolecule which chemical structure is given in Scheme 1, and the ratio of primary, secondary and ternary amine groups on PEI macromolecule chains is equal to 1:2:1 approximately [20]. In this work, polyethyleneimine was grafted onto the surfaces of micron-sized silica gel particles in the manner of "grafting onto" [21], and grafting particles PEI/SiO_2 were obtained. Afterward, the grafted PEI on SiO_2 particles was quaternized via two polymer reac-

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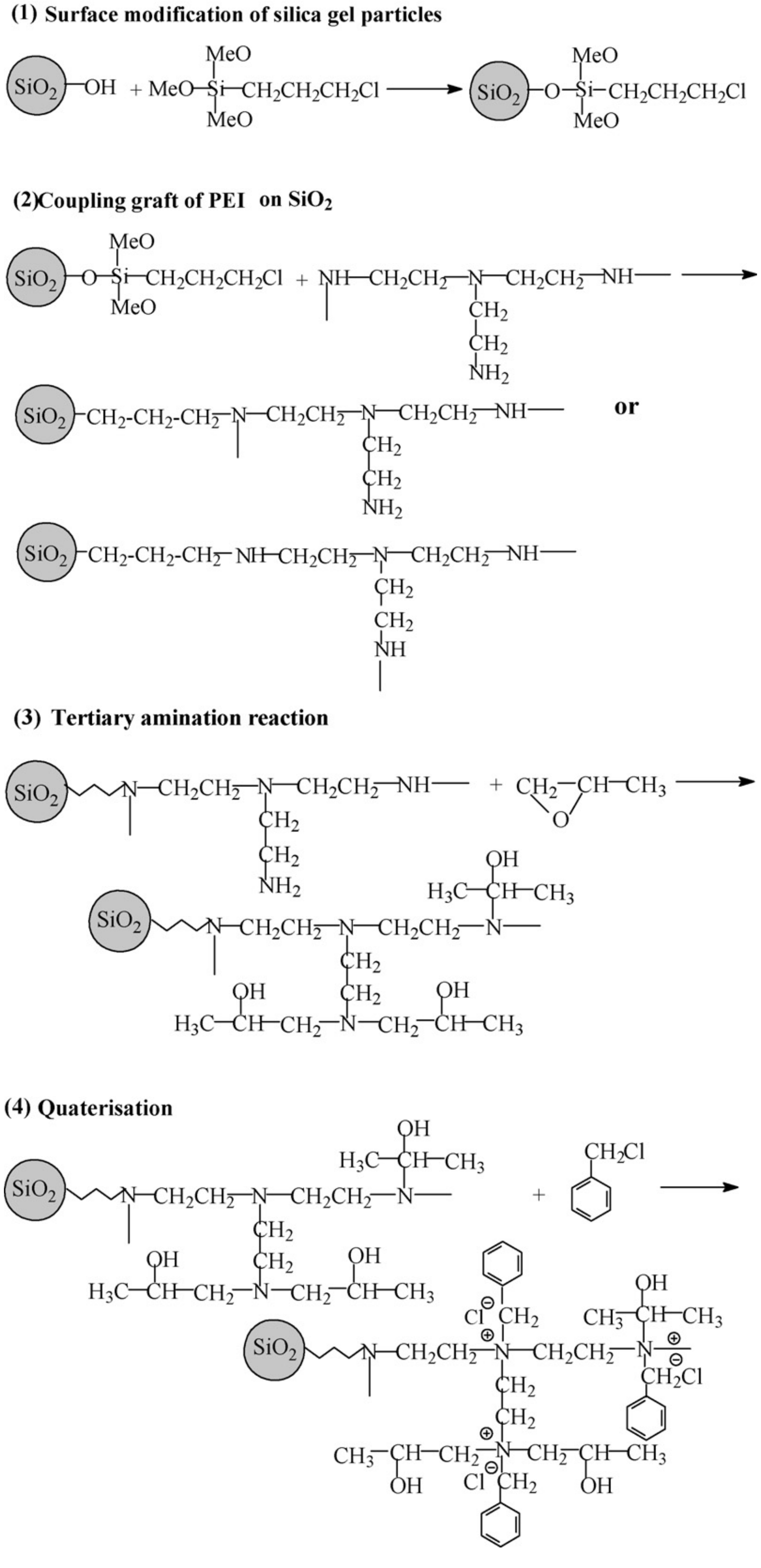

Scheme 1. Schematic representation of preparing process for QPEI/SiO_2.

tions, tertiary amination reaction and quaternisation. Finally, the functional composite particles, QPEI/SiO_2, on which a great deal of quaternary ammonium groups were supported, were prepared. The functional particles QPEI/SiO_2 were used in the adsorption and removal of chromate anions from aqueous solutions for the first time, and the adsorption mechanism was also researched. As compared with those clay minerals surface-modified with cationic surfactants [16,18], the particles QPEI/SiO_2 have much stronger adsorption ability for chromate anions owing to the high density of the cationic groups on their surfaces. In addition, the particles QPEI/SiO_2 combine well the sorption function of QPEI towards chromate anions and the excellent physicochemical properties of silica gel particles. To our knowledge, the similar study has not been reported. For the removal heavy metal ions from wastewater with the adsorption method, it is a promising route to graft functional polymer onto inorganic carriers to prepare solid adsorbents with high performance.

2. Experiments

2.1. Materials and instruments

Silica gel (120–160 mesh, about 125 μm of diameter, specific area of 350 m^2/g, pore size of 6 nm, Ocean Chemical Limited Company, Qingdao, in China) was received, and γ-chloropropyl trimethoxysilane (CPMS, Yongchang Chemical Limited Company, Naking in China) was of analytical grade. Polyethyleneimine ($Mr = 2 \times 10^4 \sim 5 \times 10^4$, aqueous solution with a content of 35%, Qianglong Chemical Limited Company, Wuhan in China) was of chemical grade and its concentration was determined accurately with UV spectrophotometry before use. Epihydrin (Beijing Chemical Reagent Company) was of analytical grade. Benzyl chloride was of analytical grade and was purchased from Chinese Reagent Company. 1,5-Diphenylcarbazide (Guangfu Refinement Reagent Institute, Tianjin, China) and potassium chromate and were all of analytical grade.

Used instruments were as follows: 8400S Shimadzu FTIR spectrometer, Unic-2602 UV spectrometer (American Unic Company), and PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai), an electrophoresis instrument (Najing University Institute of Applying Physics, China) and THZ-82 constant temperature shaker equipped with water bath (Shanghai Boxun Medical Apparatus Plant, China).

2.2. Preparation and characterization of grafting particle PEI/SiO_2

Based on the previous study [21], the grafting particles PEI/SiO_2 were prepared, and the typical procedure is as follows. Silica gel particles activated with the aqueous solution of methane sulfonic acid were reacted with γ-chloropropyl trimethoxysilane (CPMS) in xylene (as solvent) at 80 °C for 6 h, resulting in the surface-modified silica gel particles, denoted as CP-SiO_2. A certain amount of CP-SiO_2 particles were added into the PEI solution, and the content was allowed to react at a refluxing temperature of 95 °C for 8 h. After ending the reaction, the product particles were washed repeatedly with distilled water to remove un-reacted PEI, filtrated, and dried under vacuum, resulting in the grafting particles PEI/SiO_2. The PEI grafting degree of the particles PEI/SiO_2 was determined with acid–base titration method. The PEI/SiO_2 particles weighted accurately were soaked in water and were swollen fully. This aqueous mixture was titrated using HCl standard solution. The used particles of PEI/SiO_2 in this work have a PEI grafting degree of 8.4 g/100 g. The infrared spectrum of PEI/SiO_2 was determined with KBr pellet method to confirm its chemical structure.

2.3. Preparation and characterization of functional particle QPEI/SiO_2

Tertiary amination reaction was first performed. 5 g of PEI/SiO_2 was added into a glass reactor and swollen in ethanol for 4 h. The content of the primary and secondary amine groups on the added PEI/SiO_2 particles was approximately calculated according to the grafting degree determined. Epihydin as alkylation agent, with an amount (mol) of 10 times more than the amount of the primary and the secondary amine groups of the grafted PEI was added. The mixture was allowed to react under stirring for 8 h in an ice-water bath because the tertiary amination is a strong exothermic reaction. After finishing the tertiary amination reaction, the product particles (TPEI/SiO_2) were filtered off, washed with distilled water and dried under vacuum to constant weight.

Afterward, the quaterisation was carried out. Particles TPEI/SiO_2 swollen in ethanol for 4 h were allowed to be quaternized at 50 °C for a certain period of time by using benzyl chloride as quaterisation agent. The product particles (QPEI/SiO_2) were filtered off, washed with ethanol and dried under vacuum to constant weight. Actually, the particles QPEI/SiO_2 also can be considered as a functional grafting particle on which polyelectrolyte QPEI (a polymeric quaternary ammonium salt) is grafted.

To effectively control the tertiary amination and quaterisation reaction of the grafted PEI in this work, those reaction conditions of tertiary amination and quaterisation reaction of the line-type PEI in our previous study [22] were referenced. By controlling quaterisation reaction time, the functional particles QPEI/$SiO_2$with different quaterisation degrees were obtained. The quaterisation degree (mmol/g) implies the millimole number of the quaternary ammonium groups per gram of QPEI/SiO_2 particles. It was determined by using silver nitrate titration method in which the QPEI/SiO_2 particles fully swollen in water was titrated using $AgNO_3$ standard solution (Cl^- ions of the quaternary ammonium salt of QPEI/SiO_2 were reacted with Ag+ ions of $AgNO_3$). The chemical structure of QPEI/SiO_2 was characterized with infrared spectrum. The zeta potential of QPEI/SiO_2 particles was determined, and the detailed procedure is as follows. A suspension of QPEI/SiO_2 particles was prepared, stirred fully, and then it was allowed to stand statically. The supernatant (actually, the supernatant was also a suspension, only exiguous particles of QPEI/SiO_2 were dispersed in the aqueous medium) was withdrawn, and the zeta potential of QPEI/SiO_2 particle was determined with an electrophoresis instrument.

2.4. Examining adsorption property of QPEI/SiO_2 for chromate anions

2.4.1. Examining adsorption kinetics behaviour of QPEI/SiO_2 for chromate ions

A given volume of K_2CrO_4 solution with a concentration of 0.1 g/L was placed in a conical flask with a plug, and 0.2 g of QPEI/SiO_2 particles accurately weighted was added into this solution. The flask was shaken on a constant temperature shaker at 30 °C. At a fixed time intervals, samples of the solution were withdrawn from the flask content, and were separated centrifugally. The concentrations of $CrO_4{}^{2-}$ ion in the supernatants were determined spectrophotometrically at 540 nm by using a double beam UV–vis spectrophotometer after complexation with 1,5-diphenyl carbazide [23] and the adsorption amounts were calculated. The adsorption amount as a function of time was plotted, the adsorption rate was estimated, and the time in which the adsorption reached equilibrium was determined. For the comparison, the adsorption kinetics behaviour of the grafting particles PEI/SiO_2 was also examined.

2.4.2. Isothermal adsorption experiment

The isothermal adsorption experiments were carried out in batch mode at different temperatures in a range of 25–50 °C. 50 mL of K_2CrO_4 solution in a concentration range of 0.01–0.10 g/L was transferred into several conical flasks of 150 mL, respectively. 0.02 g of QPEI/SiO_2 particles weighted accurately was added into these solutions. These mixtures were placed on a shaker and shaken for 70 min to reach adsorption equilibrium. These mixtures were separated centrifugally, and the equilibrium concentrations of $CrO_4{}^{2-}$ ion in the supernatants were determined. The equilibrium adsorption amounts Q_e(g/g) were calculated according to Eq. (1), and the relationship curves between equilibrium adsorption amounts and equilibrium concentrations were figured, namely, isothermal adsorption curves were plotted.

$$Q_e = \frac{V(C_0 - C_e)}{m \times 1000} \qquad (1)$$

where, C_0 and C_e (g/L) are the initial and equilibrium concentrations of $CrO_4{}^{2-}$ ion, respectively, V (mL) is the volume of the adsorption solution, and m (g) is the mass of the functional particles $QPEI/SiO_2$.

2.4.3. *Examining effects of various factors on adsorption capacity of QPEI/SiO$_2$*

The isothermal adsorption experiments were carried out at different medium pH values to research the effect of pH value of the medium on the adsorption capacity of the functional particles $QPEI/SiO_2$; the isothermal adsorption experiments were also conduced by using the $QPEI/SiO_2$ particles with different quaterisation degrees so as to research the effect of the quaterisation degree on the adsorption capacity of the functional particles; The effect of temperature on the adsorption capacity of the functional particles $QPEI/SiO_2$ was also examined.

2.5. *Desorption experiments*

A given amount of $QPEI/SiO_2$ particles adsorbing $CrO_4{}^{2-}$ ions in a saturation state was packed into a piece of glass pipe with an internal diameter of 0.8 cm, and the bed volume (BV) of the packed column was 2 mL. A NaOH solution of 0.1 M and a mixed solution of NaOH and NaCl, whose concentrations were 0.1 and 0.5 M, respectively, were used as eluent, respectively. The eluent was allowed to flow gradually through the column at a rate of two bed volumes per hour (2BV/h) in countercurrent manner. The effluent with two-volume (2BV) interval was collected, and the concentration of $CrO_4{}^{2-}$ ion of the collected effluent was determined with spectrophotometry. The dynamic desorption curve was plotted, and elution property f $QPEI/SiO_2$ particles adsorbed $CrO_4{}^{2-}$ ions was estimated.

3. Results and discussions

3.1. *Reaction process to prepare composite particles QPEI/SiO$_2$*

γ-Chloropropyl trimethoxy silane (CPMS) was selected as coupling agent to chemically link silica gel with polyethyleneimine. In the surface-modification reaction of silica gel particles, the silanol groups on the activated silica gel particles were reacted with CPMS, and the surface-modified silica gel particles ($CP\text{-}SiO_2$) were formed. Subsequently, $CP\text{-}SiO_2$ particles were reacted with PEI and the grafting particles PEI/SiO_2 were obtained. Afterward, by using epihydrin as tertiary amination agent, the primary and secondary amine groups on the chains of the grafted PEI were transferred into tertiary amine groups. In the tertiary amination reaction, ring-opening reaction for epihydrin and alkylation reaction for the primary and secondary groups of the grafted PEI occur synchronously. Finally, those tertiary amine groups were transferred into quaternary ammonium groups through quaternisation by using benzyl chloride as quaternisation agent, resulting in $QPEI/SiO_2$ particles. All the reaction processes to prepare the functional particles, $QPEI/SiO_2$, are expressed schematically in Scheme 1.

3.2. *Chemical structure of QPEI/SiO$_2$*

Fig. 1 shows the infrared spectra of four particles, SiO_2, $CP\text{-}SiO_2$, PEI/SiO_2 and $QPEI/SiO_2$. After modification of silica gel particles by coupling agent CPMS, the vibration absorption of C–H bond at 2958 and 2848 cm^{-1}as well as in the range of 1383–1440 cm^{-1} have appeared. They indicate that $-CH_2$ and $-CH_3$ groups have been produced on the surface of silica gel, the reaction between CPMS and silanol groups has occurred, and particles $CP\text{-}SiO_2$ has formed. After the reaction of $CP\text{-}SiO_2$ with PEI, the stretching vibration and bending vibration absorptions of N–H bond appear at 3641and 1701 cm^{-1}, respectively. Besides, the produced bands at 1488 and1560 cm^{-1} are ascribed to the stretching vibration absorption of C–N bond. The appearances of these bands reveal that the macromolecular chains of PEI have chemically linked onto the surfaces of silica gel particles in coupling manner, and the grafting particles PEI/SiO_2 have been formed. In the spectrum of $QPEI/SiO_2$, the characteristic absorptions of benzene rings have been appeared at 1650, 1507, 1454 and 702 cm^{-1}, and they are attributed to the benzyl groups linked to the N atoms of the quaternary ammonium groups. The appearances of the above bands show that the quaterisation of the grafted PEI has occurred, and the composite particles $QPEI/SiO_2$ have been obtained.

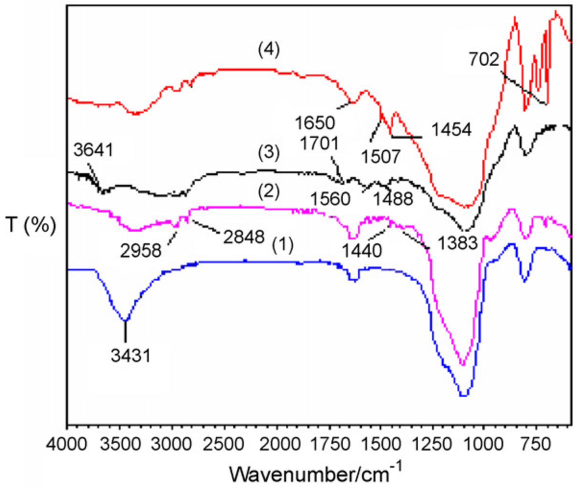

Fig. 1. FTIR spectra of various particles, (1) SiO_2; (2) $CP\text{-}SiO_2$; (3) PEI/SiO_2; (4) $QPEI/SiO_2$.

3.3. *Adsorption behaviour of functional particles QPEI/SiO$_2$ for chromate ions*

3.3.1. *Adsorption kinetics curve*

In Fig. 2, the adsorption kinetics curve of the functional particles $QPEI/SiO_2$ towards chromate ions is displayed. Simultaneously,

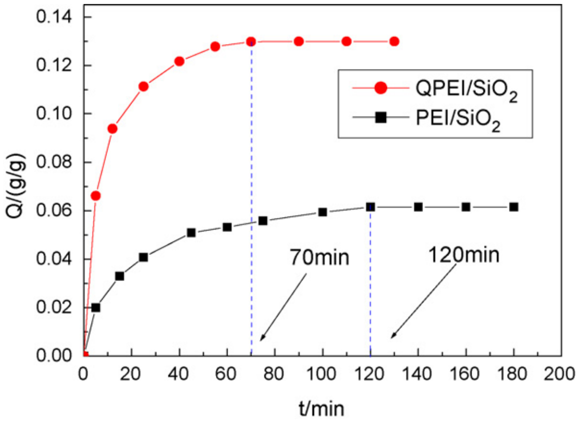

Fig. 2. Adsorption kinetic curves of $QPEI/SiO_2$ and PEI/SiO_2 particles for of chromate anions. Temperature: 30 °C; pH 7.

for the comparison purpose, the adsorption kinetics curve of the grafting particles PEI/SiO_2 is also shown in Fig. 2. It can be seen from Fig. 2 that for the functional particles QPEI/SiO_2, only 70 min is needed to reach adsorption equilibrium, whereas for grafting particles PEI/SiO_2, 120 min is needed. The grafted QPEI is a polyelectrolyte, and there is a great deal of quaternary ammonium ions on the surfaces of articles QPEI/SiO_2. By right of the hydration of the quaternary ammonium ions, The QPEI chains on QPEI/SiO_2 are easer to be fully swollen than PEI chains on PEI/SiO_2. The fully stretching macromolecular chains on QPEI/SiO_2 can reduce the mass transfer resistance and facilitate the diffusion of $CrO_4{}^{2-}$ anions into the inner of the polymer layer on QPEI/SiO_2 particles. Therefore, $CrO_4{}^{2-}$ anions are easy to diffuse to the sites of quaternary ammonium ions on QPEI/SiO_2 particles and are absorbed, leading to more rapid adsorption rate.

3.3.2. Adsorption isotherm

The adsorption isotherm of QPEI/SiO_2 particles with a quaterisation degree of 0.69 mmol/g at 30 °C for $CrO_4{}^{2-}$ ion is shown in Fig. 3. It can be observed that at the beginning stage, the equilibrium adsorption amount of QPEI/SiO_2 increases rapidly with the increase of the equilibrium concentration of $CrO_4{}^{2-}$ ions. When the equilibrium concentration achieves a certain value, the adsorption amounts do not change significantly, and it imply that the adsorption has reached saturation (the saturated adsorption amount is as high as about 0.143 g/g). It is obvious that the adsorption isotherms have the characteristic of Langmuir-type isotherms. According to the reciprocal form of Langmuir equation as shown in Eq. (2), $1/Q_e$ as a function of $1/C_e$ is figured, and a fine straight line with a correlation coefficient of 0.999 is obtained as shown in Fig. 4.

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_d Q_m} \times \frac{1}{Ce} \qquad (2)$$

where K_d is the Langmuir constant of the system and Q_m is the theoretical maximum adsorption capacity. The obtained Q_m is equal to 0.152 g/g, and it is closed to the experimental value (0.143 g/g), indicating the Langmuir model is very appropriate for the experimental data.

The high adsorption capacity (0.143 g/g) should be attributed to the strong interaction between QPEI/SiO_2 particles and $CrO_4{}^{2-}$ ions. In aqueous solution, the grafted polyelectrolyte molecules of QPEI dissociate to produce a mass of quaternary ammonium cations, and the very high density of positive charge on the surfaces of QPEI/SiO_2 particles is leaded to. Therefore, a very strong electrostatic interaction between QPEI/SiO_2 particles and $CrO_4{}^{2-}$ ions is produced, leading to the very strong adsorption ability of QPEI/SiO_2 particles towards $CrO_4{}^{2-}$ ions.

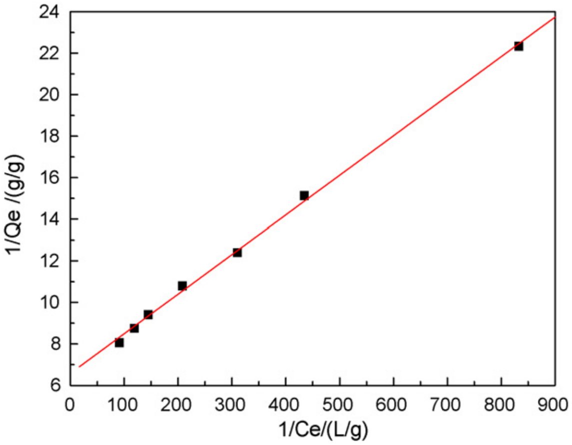

Fig. 4. Relationship straight line between $1/Q_e$ and $1/C_e$.

3.4. Effects of various factors on adsorption capacity of QPEI/SiO_2

3.4.1. Effect of quaterisation degree

The adsorption isotherms of QPEI/SiO_2 particles with different quaterisation degrees in neutral solution are given in Fig. 5. It can be seen clearly that the adsorption capacity of QPEI/SiO_2 is increased with the enhancement of the quaterisation degree of QPEI/SiO_2 particles. As described above, the driving force for the adsorption of QPEI/SiO_2 particles towards $CrO_4{}^{2-}$ ions is the electrostatic interaction. As the quaterisation degree of QPEI/SiO_2 particles is enhanced, the number of the quaternary ammonium cations on the surfaces of QPEI/SiO_2 particles will increase, resulting in the increase of the adsorption capacity.

It can be also found from Fig. 5 that the grafting particles PEI/SiO_2, on which the grafted PEI chains are un-quaternized, still has some certain adsorption action for $CrO_4{}^{2-}$ ions, as shown by the nethermost curve in Fig. 5. The reason for this is as follows. There is a great deal of N atoms of amine groups on PEI chains. As pH < 10, the most of these N atoms of amine groups of PEI in aqueous solution exist in protonated states, so PEI can be also seen as a cationic polyelectrolyte [20,24], and some adsorption action of particles PEI/SiO_2 towards $CrO_4{}^{2-}$ ions will be produced by right of electrostatic interaction. However, the protonated degree of PEI decreases with the increase of pH value of the medium, and in neutral solution, only 60% of N atoms of amine groups exist in protonated states [20], leading to the lower adsorption capacity of PEI/SiO_2 particles in comparison with QPEI/SiO_2 particles.

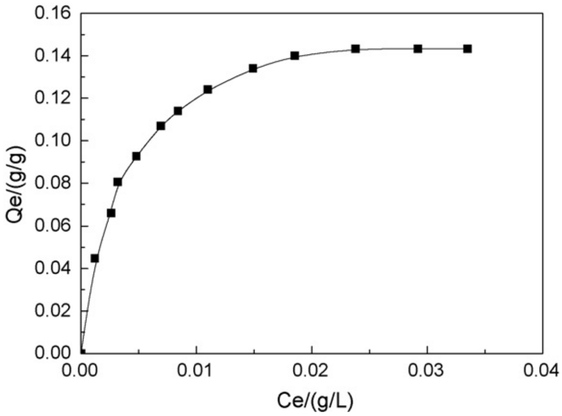

Fig. 3. Adsorption isotherm of QPEI/SiO_2 towards chromate anions. Quaterination degree of QPEI/SiO_2: 0.91 mmol/g; Temperature: 30 °C; pH 7.

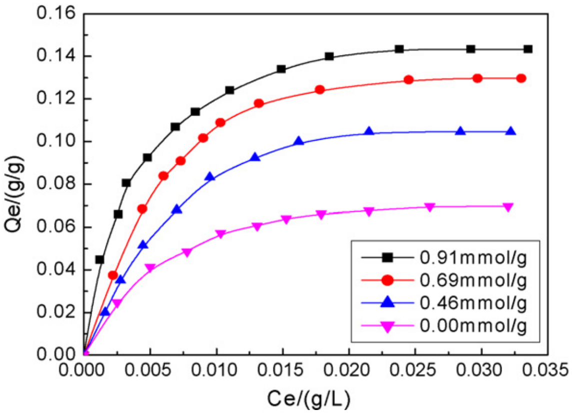

Fig. 5. Adsorption isotherms of QPEI/SiO_2 with different quaterisation degrees. Temperature: 30 °C; pH 7.

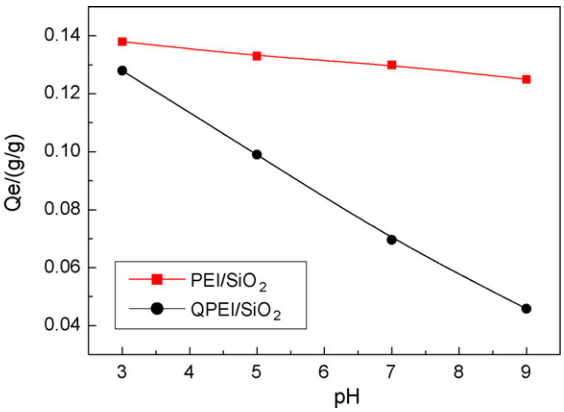

Fig. 6. Effect of pH value of medium on adsorption property of two kinds of particles. Temperature: 30 °C; Quaterination degree of QPEI/SiO$_2$: 0.69 mmol/g; Grafting degree of PEI/SiO$_2$: 8.4 g/g.

3.4.2. Effect of pH value

In Fig. 6, the relationship curve between saturated adsorption amounts of QPEI/SiO$_2$ particles for CrO_4^{2-} ions and pH values (the initial pH values of the chromate solutions) is displayed, and it derived from the adsorption isotherms of QPEI/SiO$_2$ particles at different pH values. The corresponding curve of PEI/SiO$_2$ particles is also given in Fig. 6. According to the disassociation equilibrium of Cr(VI) species in aqueous solution, $Cr_2O_7^{2-}$ ions with strong oxidizing property will be produced as pH is lower and the concentration of chromate salt is greater. In order to avoid the formation of $Cr_2O_7^{2-}$ ions with strong oxidizing property, the lower limit of pH is selected as pH = 3. The following facts can be seen from Fig. 6. The adsorption capacity of QPEI/SiO$_2$ particles towards CrO_4^{2-} ions is affected slightly by pH value, and it has a little decrease with increasing pH value. The reason for this is that there still is a part of un-quaternized N atoms of amine groups on the grafted QPEI chains. 70% of them are protonated in acidic solution [20]. However, their protonated extent decreases with the increase of pH value, resulting in a little decrease of the adsorption capacity of QPEI/SiO$_2$ particles with increasing pH value. Despite all this, the quaternary ammonium cations are the main contributor for the adsorption action of QPEI/SiO$_2$ particles towards CrO_4^{2-} ions, whereas the adsorption action coming from the protonated N atoms of amine groups is miner. Therefore, the adsorption capacity of QPEI/SiO$_2$ particles is affected by pH value very slightly. In other words, the adsorption action of QPEI/SiO$_2$ particles towards CrO_4^{2-} ions is independent on pH value of the medium basically.

Whereas the adsorption capacity of PEI/SiO$_2$ particles is affected greatly by pH value, namely, the adsorption property of PEI/SiO$_2$ particles towards CrO_4^{2-} ions is dependent on pH value of the medium. As described above, in acidic solution, 70% of N atoms of amine groups of PEI are protonated, so PEI/SiO$_2$ particles have higher adsorption capacity in acidic solution. The adsorption capacity decreases continually with increasing pH value due to the decrease of the protonated extent of N atoms. As pH = 9, the protonated extent will be decrease to 32% [20]. Therefore, the adsorption capacity of PEI/SiO$_2$ particles in neutral solution, especially in basic solution, will be decreased to a very low level. The adsorption properties of other amine group-modified adsorbents are also dependent on pH value like as the behaviour of PEI/SiO$_2$ particles.

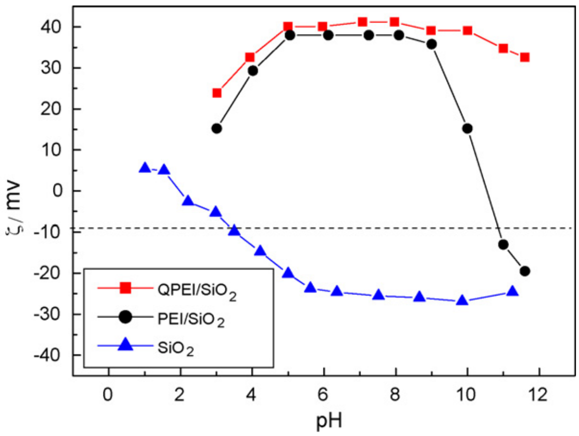

Fig. 7. Zeta potential curves of three kinds of particles.

The zeta potential curves of the three particles, QPEI/SiO$_2$, PEI/SiO$_2$ and SiO$_2$, are shown in Fig. 7. Via analyzing these zeta potential curves, the pH independence of the adsorption action of QPEI/SiO$_2$ particles towards CrO_4^{2-} ions and the pH dependence of the adsorption action of PEI/SiO$_2$ particles can be further demonstrated. It can be seen from Fig. 7 that after grafting PEI, the zeta potential of SiO$_2$ transforms from negative value into positive value. This fully displays the cationic characteristic of PEI macromolecules. The following important facts can be found from Fig. 6: (1) The zeta potential of QPEI/SiO$_2$ particles is higher than that of PEI/SiO$_2$ particles, indicating there is higher positive charge density on the surface of QPEI/SiO$_2$ particles than on that of PEI/SiO$_2$ particles. (2) After pH > 8, the zeta potential of PEI/SiO$_2$ particles declines sharply with the increase of pH value, whereas the zeta potential of QPEI/SiO$_2$ does not change nearly. This fully displays the pH sensitivity of the cationic characteristic of PEI and the pH independence of the cationic characteristic of QPEI. (3) As pH = 10.3, the zeta potential of PEI/SiO$_2$ has declined to zero, namely, the isoelectric point of PEI/SiO$_2$ is equal to 10.3, and this is very consistent with the literature value [20]. At this point, the grafting particles PEI/SiO$_2$ have lost the adsorption ability for CrO_4^{2-} ions completely, whereas QPEI/SiO$_2$ particles still can hold high adsorption capacity for CrO_4^{2-} ions.

3.4.3. Effect of temperature

The adsorption experiments were performed at different temperatures, and the adsorption isotherms at various temperatures are determined, and the saturated adsorption amounts as a function of temperature are shown in Fig. 8. It is obvious that the adsorption capacity of QPEI/SiO$_2$ particles decreases with raising temperatures. The adsorption action originating from the electrostatic interaction is a physical adsorption action, and the adsorption process is an exothermic process. Thus, the decrease of the adsorption capacity with enhancing temperatures will be resulted in.

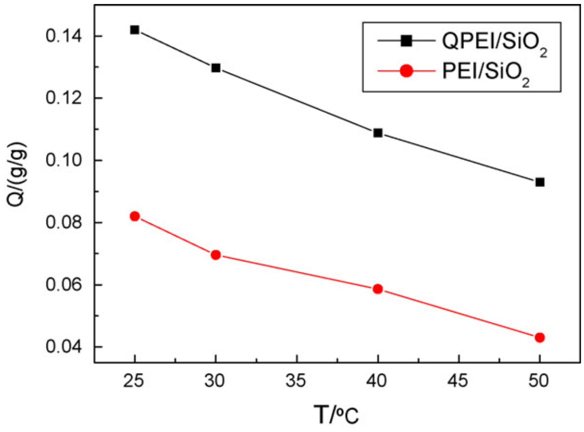

Fig. 8. Effect of temperature on adsorption property of two kinds of particles.

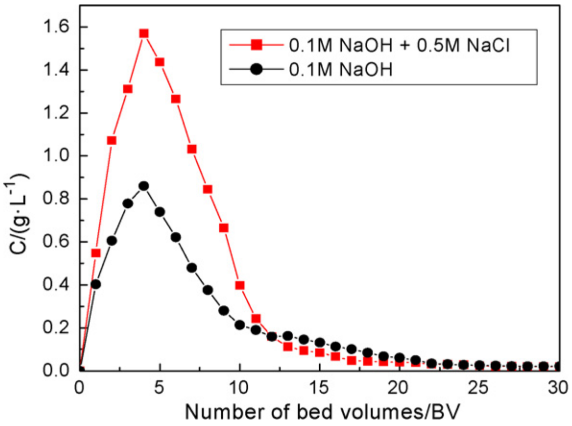

Fig. 9. Elution curves of chromate anions on QPEI/SiO_2 column.

3.5. *Desorption property*

An effective solid adsorbent used in the wastewater treatment not only needs to possess high adsorption capacity for those harmful substances, but also needs to have good regeneration property. The dynamic desorption experiments for QPEI/SiO_2 particles adsorbing $CrO_4{}^{2-}$ ions in a saturated state were conduced by using NaOH aqueous solution and a mixed solution of NaOH and NaCl as eluents, respectively. The dynamic desorption curves are given in Fig. 9.

It can be seen from Fig. 9 that the desorption curve using alone NaOH solution as eluent locates below the desorption curve using the mixed solution as eluent. The calculation result shows the following contrastive data. As used NaOH solution as eluent, the desorption ratio in 30 bed volumes (BV) only reaches 66.3%. Whereas as used the mixed solution of NaOH and NaCl as eluent, the desorption ratio in 30 BV actually reaches 97.3%. The difference is caused by different desorption mechanisms. NaCl solution plays a role of ion-exchange ($CrO_4{}^{2-}$ ion is exchanged by Cl^- ion) and can effectively elute $CrO_4{}^{2-}$ ions from the cationic surfaces of QPEI/SiO_2 particles, whereas NaOH solution mainly plays a role of de-protonation for those un-quaternized N atoms of amine groups of QPEI/SiO_2 particles. The combination of the two actions enables $CrO_4{}^{2-}$ ions to be desorbed substantially, so high elution efficiency is resulted in as the mixed solution of NaOH and NaCl is used as eluent. As NaOH solution is solely used, the absorbed $CrO_4{}^{2-}$ ions on QPEI/SiO_2 particles cannot be eluted well because of the poorer ion exchange ability of OH^- anions than that of Cl^- anions. The above experimental result shows that QPEI/SiO_2 particles have excellent eluting and regenerating property as long as appropriate eluents are used.

4. Conclusions

In this work, polyethyleneimine was grafted on the surfaces of micro-sized silican gel particles, subsequently, via two polymer reactions, tertiary amination reaction and quaterisation, functional composite particles QPEI/SiO_2, on which a great deal of quaternary ammonium groups were supported, were prepared. Actually, particles QPEI/SiO_2 can be considered as a kind of functional silica gel particles on which polyelectrolyte QPEI (polymeric quaternary ammonium salt) is grafted. The functional particles QPEI/SiO_2 have strong adsorption ability for chromate anions by right of electrostatic interaction. The adsorption ability of particles QPEI/SiO_2 towards chromate anions depends on the quaterisation degree of the grafted PEI greatly, and the particles QPEI/SiO_2 with higher quaterisation degrees have stronger adsorption capacities. Furthermore, the adsorption ability of particles QPEI/SiO_2 is not nearly dependent of pH values of the medium. The particles QPEI/SiO_2 have fine elution property, namely, excellent regeneration property. As used the mixed solution of NaOH and NaCl as an eluent, the adsorbed $CrO_4{}^{2-}$ ions on particles QPEI/SiO_2 are easy to be eluted. The functional particles QPEI/SiO_2 combine well the affinity of QPEI for chromate anions and the excellent properties of micro-sized silica gel particles, and this kind of functional composite particles is promising in the actual water treatment to remove chromate anions from industrial wastewater.

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