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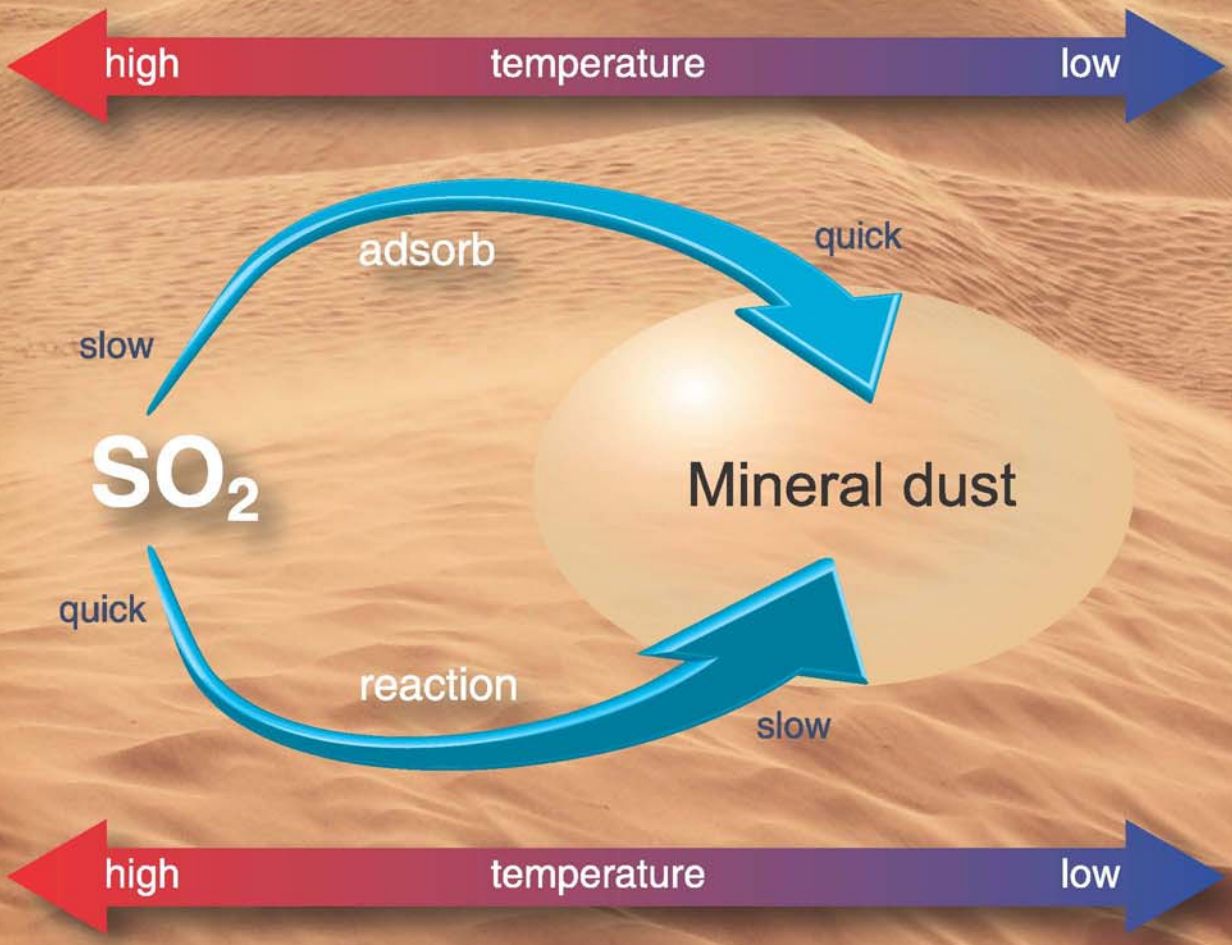

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2369 Effects of seasonal climatic variability on several toxic contaminants in urban lakes: Implications for the impacts of climate change
Qiong Wu, Xinghui Xia, Xinli Mou, Baotong Zhu, Pujun Zhao, and Haiyang Dong

2379 Preparation of cross-linked magnetic chitosan with quaternary ammonium and its application for Cr(VI) and P(V) removal
Wei Yao, Pinhua Rao, Irene M.C. Lo, Wenqi Zhang, and Wenrui Zheng

2387 Formation pathways of brominated products from benzophenone-4 chlorination in the presence of bromide ions
Ming Xiao, Dongbin Wei, Liping Li, Qi Liu, Huimin Zhao, and Yuguo Du

2397 Influence of the inherent properties of drinking water treatment residuals on their phosphorus adsorption capacities
Leilei Bai, Changhui Wang, Liansheng He, and Yuansheng Pei

2406 Radiation induced decomposition of a refractory cefathiamidine intermediate
Qiburi Bao, Lujun Chen, and Jianlong Wang

2412 Characterization of aerosol optical properties, chemical composition and mixing states in the winter season in Shanghai, China
Yong Tang, Yuanlong Huang, Ling Li, Hong Chen, Jianmin Chen, Xin Yang, Song Gao, and Deborah S. Gross

2423 Knudsen cell and smog chamber study of the heterogeneous uptake of sulfur dioxide on Chinese mineral dust
Li Zhou, Weigang Wang, Yanbo Gai, and Maofa Ge

2434 Experimental study on filtration and continuous regeneration of a particulate filter system for heavy-duty diesel engines
Tao Tang, Jun Zhang, Dongxiao Cao, Shijin Shuai, and Yanguang Zhao

2440 Combination of heterogeneous Fenton-like reaction and photocatalysis using Co-TiO_2 nanocatalyst for activation of $KHSO_5$ with visible light irradiation at ambient conditions
Qingkong Chen, Fangying Ji, Qian Guo, Jianping Fan, and Xuan Xu

2451 Atmospheric sulfur hexafluoride *in-situ* measurements at the Shangdianzi regional background station in China
Bo Yao, Lingxi Zhou, Lingjun Xia, Gen Zhang, Lifeng Guo, Zhao Liu, and Shuangxi Fang

2459 Direct radiative forcing of urban aerosols over Pretoria (25.75°S, 28.28°E) using AERONET Sunphotometer data: First scientific results and environmental impact
Ayodele Joseph Adesina, Kanike Raghavendra Kumar, Venkataraman Sivakumar, and Derek Griffith

2475 Chemical characteristics and source apportionment of atmospheric particles during heating period in Harbin, China
Likun Huang and Guangzhi Wang

2484 Microbial community structures in an integrated two-phase anaerobic bioreactor fed by fruit vegetable wastes and wheat straw
Chong Wang, Jiane Zuo, Xiaojie Chen, Wei Xing, Linan Xing, Peng Li, Xiangyang Lu, and Chao Li

2493 Persistent pollutants and the patchiness of urban green areas as drivers of genetic richness in the epiphytic moss *Leptodon smithii*
Valeria Spagnuolo, Flavia De Nicola, Stefano Terracciano, Roberto Bargagli, Daniela Baldantoni, Fabrizio Monaci, Anna Alfani, and Simonetta Giordano

CONTENTS

2500 Enhanced removal of ethylbenzene from gas streams in biotrickling filters by Tween-20 and Zn(II)
Lu Wang, Chunping Yang, Yan Cheng, Jian Huang, Haining Yang, Guangming Zeng, Li Lu, and Shanying He

2508 Enhanced efficiency of cadmium removal by *Boehmeria nivea* (L.) Gaud. in the presence of exogenous citric and oxalic acids
Huaying Li, Yunguo Liu, Guangming Zeng, Lu Zhou, Xin Wang, Yaqin Wang, Chunlin Wang, Xinjiang Hu, and Weihua Xu

2517 Comparative sorption and desorption behaviors of PFHxS and PFOS on sequentially extracted humic substances
Lixia Zhao, Yifeng Zhang, Shuhong Fang, Lingyan Zhu, and Zhengtao Liu

2526 Inhibitory effects of nisin-coated multi-walled carbon nanotube sheet on biofilm formation from *Bacillus anthracis* spores
Xiuli Dong, Eric McCoy, Mei Zhang, and Liju Yang

2535 A comparative study and evaluation of sulfamethoxazole adsorption onto organo-montmorillonites
Laifu Lu, Manglai Gao, Zheng Gu, Senfeng Yang, and Yuening Liu

2546 Removal of formaldehyde over $Mn_xCe_{1-x}O_2$ catalysts: Thermal catalytic oxidation *versus* ozone catalytic oxidation
Jia Wei Li, Kuan Lun Pan, Sheng Jen Yu, Shaw Yi Yan, and Moo Been Chang

2554 Humic acid transport in saturated porous media: Influence of flow velocity and influent concentration
Xiaorong Wei, Mingan Shao, Lina Du, and Robert Horton

2562 Salinity influence on soil microbial respiration rate of wetland in the Yangtze River estuary through changing microbial community
Xue Fei Xi, Lei Wang, Jia Jun Hu, Yu Shu Tang, Yu Hu, Xiao Hua Fu, Ying Sun, Yiu Fai Tsang, Yan Nan Zhang, and Jin Hai Chen

2571 Comments on “Adsorption of 2-mercaptobenzothiazole from aqueous solution by organo-bentonite” by P. Jing, M.H. Hou, P. Zhao, X.Y. Tang, H.F. Wan
Yuhshan Ho

2573 Reply to comments on “Adsorption of 2-mercaptobenzothiazole from aqueous solution by organo-bentonite” by Yuhshan Ho
Ping Jing, Meifang Hou, Ping Zhao, Xiaoyan Tang, and Hongfu Wan

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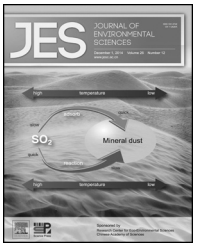

Preparation of cross-linked magnetic chitosan with quaternary ammonium and its application for Cr(VI) and P(V) removal

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ABSTRACT

Pollutants that exist in anionic species are issues of concern in water treatment. Compared to cationic pollutants, the removal of anionic pollutants by adsorption is more difficult because most adsorbents carry predominantly negative charges in neutral and alkaline environments. In this study, a cross-linked chitosan derivative with quaternary ammonium and magnetic properties (QM-chitosan) was prepared and employed to remove chromium(VI) and phosphorus(V) (Cr(VI) and P(V)) from aqueous environments. The QM-chitosan was characterized by Fourier transform infrared spectrometry (FT-IR), thermogravimetric analysis (TGA), energy dispersive X-ray (SEM-EDX) and zeta potential. Batch experiments show that QM-chitosan can effectively remove Cr(VI) and P(V), and the main mechanism was believed to be electrostatic interaction. A pseudosecond-order model was fitted to describe the kinetic processes of Cr(VI) and P(V) removal. The adsorption isotherms of both Cr(VI) and P(V) on the QM-chitosan were well fitted by the Langmuir isotherm equation. The saturated adsorption capacity of P(V) (2.783 mmol/g) was found to be higher than that of Cr(VI) (2.323 mmol/g), resulting from the size of the $H_2PO_4^-$ ions being smaller than that of the $HCrO_4^-$ ions. However, the theoretical calculation and experimental results showed that QM-chitosan had a stronger affinity for Cr(VI) than P(V). The adsorption–desorption of the QM-chitosan was evaluated, and high regeneration rates were demonstrated.

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Introduction

Water pollution has become an issue of wide concern in China owing to the rapid industrialization and the increasing reliance on chemicals in the last few decades. Different methods such as redox (Brodie et al., 2011), precipitation (Golder et al., 2011), coagulation (Wang et al., 2013a), membrane separation (Ma et al., 2013) and adsorption (Pan et al., 2013) have been employed for the removal of pollutants from wastewater and drinking water. Among these methods, adsorption is often recognized as an effective and economic way to remove pollutants from water bodies, due to its simplicity, reliability and safeness. Chitosan (Ngah et al., 2011), lignocellulose (Ye et al., 2010), reed (Baidas et al., 2011), starch (Dong et al., 2010), natural minerals (Aredes et al., 2012) have been reported as useful adsorbents. Chitosan has drawn more attention due to its low cost, non-toxicity, antimicrobial properties and high adsorption potential (Laus et al., 2010; Yang et al., 2011). Some agents such as glutaraldehyde (Pratt et al., 2013), ethylene glycol diglycidyl ether (Elwakeel et al., 2013) and epichlorohydrin (Tirtom et al., 2012) have been used to

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crosslink chitosan to reinforce its chemical stability. In addition, reactive functional groups and magnetic properties were introduced into the crosslinking of chitosan, to further improve the adsorption capacity and accelerate the process of solid–liquid separation (Wang et al., 2013b; Monier et al., 2012). It was reported that multi-cyanoguanidine modified magnetic chitosan showed a high adsorption capacity for Hg(II) and could be separated easily by an external magnetic field (Wang et al., 2013b). The removal of other metal ions such as Cu(II), Cd(II) and Ni(II) by magnetic chitosan was also reported (Monier et al., 2012). Generally, to our best knowledge, target pollutants removed by chitosan primarily focused on toxic metal cations, while anionic pollutants are rarely reported.

In practice, anionic pollutants are often found in contaminated water and even become the dominant pollutants in some areas (De Lima et al., 2012). Therefore, it is important to study the removal of anionic pollutants for the protection of water environments. Few authors have studied the removal of Cr(VI) from wastewater by chitosan (Jung et al., 2013; Hu et al., 2011). The solution pH was found to significantly affect the removal efficiency of Cr(VI) due to protonization/deprotonation of chitosan. In order to effectively remove the anionic pollutants, it is necessary to prepare a chitosan which carries positive charges in a wide pH range. Quaternary ammonium salt is a typical organic compound that can ionize functional groups with positive charges and is rarely affected by the solution pH. Sowmya and Meenakshi (2014) prepared a novel quaternized chitosan–melamine–glutaraldehyde resin for the removal of nitrate and phosphate anions. Commercial quaternary ammonium salt glycidyl-trimethylammonium chloride was used for grafting on the chitosan resin, which could increase the cost of adsorbent. Thus, *in-situ* quaternization method should be favorable for the quaternization of chitosan. It is important to seek a simple and effective method to get quaternized chitosan with high charge density. Cyanuric chloride is a common chemical which contains three chlorines and shows a strong chemical activity. It is possible to obtain a chitosan derivative with high charge density by modification of cyanuric chloride and subsequent quaternization. However, related studies are rarely reported.

In this study, a quaternization pathway based on cyanuric chloride was designed to develop a chitosan derivative with quaternary ammonium. The possibility of the reactions was calculated using GAUSSIAN 03 packages (Frisch et al., 2004). Magnetic properties were also introduced into the chitosan by adding γ-Fe_2O_3 nanoparticles. Such a chitosan with quaternary ammonium and magnetic properties (QM-chitosan) was characterized and used for the removal of Cr(VI) and P(V) from aqueous solutions. The capability of QM-chitosan and the mechanisms involved in removing Cr(VI) and P(V), together with its regeneration and reusability, were investigated by conducting bench-scale experiments.

1. Materials and methods

1.1. Chemicals

Chitosan with deacetylation of 90%, cyanuric chloride (99%), triethylamine (99.5%), tetrahydrofuran (99%), acetic acid (99.5%), ammonia solution (25%), iron(II) sulfate heptahydrate (99%), iron(III) chloride anhydrous (97%), epichlorohydrin (99%), potassium bichromate (99.8%), potassium phosphate monobasic (99%) and sodium chloride (99.5%) were purchased from Aldrich Chemical or Aladdin, Ltd. All the chemicals were used without further treatment.

1.2. Preparation of magnetic nanoparticles (γ-Fe_2O_3)

A 2.93 g of $FeCl_3$ and 3.32 g of $FeSO_4{\cdot}7H_2O$ were dissolved in 80 mL of deionized water, and 10 mL of 25% $NH_3{\cdot}H_2O$ was dropwise added under vigorous stirring. Then, the solution was stirred for 1 hr. The obtained black precipitate, *i.e.*, Fe_3O_4, was washed three times with deionized water, and heated in air at 150°C for 3 hr. A brown powder was obtained and was identified as γ-Fe_2O_3 by X-ray diffraction (D2 Phaser, Bruker, Germany) analysis. Transmission electron microscopic (H-800, Hitachi, Japan) analysis indicated that the size of the γ-Fe_2O_3 precipitate was about 10 nm.

1.3. Preparation of QM-chitosan

To prepare QM-chitosan, 2.0 g of chitosan was dissolved in 100 mL of 5% acetic acid solution under vigorous stirring at 30°C for 1 hr. Then, 2.5 mL of epichlorohydrin was added into the solution for cross-linking of the chitosan. An hour later, the temperature of this system was reduced to 0°C by ice cooling, and 2.5 g of cyanuric chloride and 50 mL of tetrahydrofuran were added. The reaction was conducted under moderate agitation for 12 hr. The temperature of this system was then raised to 30°C, and 0.2 g of γ-Fe_2O_3 was added into the solution under vigorous stirring to form a uniform dispersion system. An hour later, 6.6 mL of triethylamine was added and the reaction was conducted under vigorous stirring for 12 hr to form a homogenous gel system. The gel, *i.e.*, QM-chitosan, was then washed with deionized water at least 3 times to remove the unreacted reagents. Afterwards, the QM-chitosan was dried for 12 hr under vacuum at 80°C and ground into power using a blender. The principal chemical reactions are illustrated in Fig. 1. The magnetic response property of QM-chitosan was shown in Appendix A Fig. S1, and the saturation magnetization of QM-chitosan is close to 23 emu/g (Appendix A Fig. S2), which is sufficient to be used in adsorbent separation for further recycling and reuse.

Cross-linked chitosan without quaternization and magnetic properties (C-chitosan) was also prepared using epichlorohydriny to form a chitosan gel.

1.4. Characterization of QM-chitosan

A zeta potential analyzer (Zeta-Meter 3.0+, Ankersmid, Netherlands), scanning electron microscopy with energy dispersive X-ray (SEM-EDX) (S-3400N, Hitachi, Japan) and Fourier transform infrared spectrometry (FT-IR) (AVATAR380, Nicolet, USA) were employed to analyze the surface charges, morphology, elemental components and surface functional groups of QM-chitosan and C-chitosan. In addition, thermogravimetric analysis (TGA) (PT1000, Linseis, Germany) was also conducted to determine the wt.% of magnetic particles inside the QM-chitosan and the results indicated that the mass content of γ-Fe_2O_3 in the QM-chitosan was 8%.

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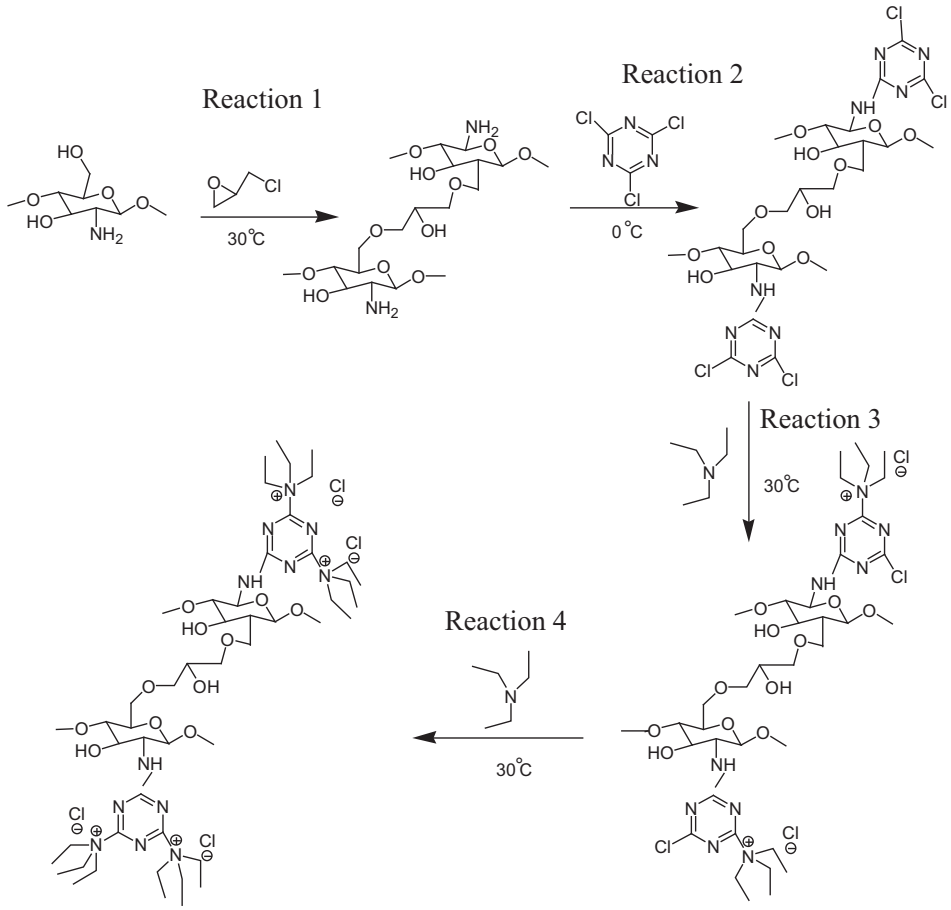

Fig. 1 – Quaternization process of chitosan.

1.5. *Batch experiments*

Experiments to investigate Cr(VI) adsorption by QM-chitosan, including studies of the adsorption kinetics and isotherms, and the effects of pH, coexisting ions and ionic strength, were conducted using 50-mL glass vials with screw caps containing Teflon-lined rubber septa. Briefly, a certain amount of QM-chitosan and 40 mL of Cr(VI) solution with the desired pH and concentration were mixed in 50-mL glass vials and then shaken in an end-over-end manner at 26 r/min and at 25 ± 1°C. After a predefined reaction time, the solutions in the vials were quickly filtered through 0.45-μm membranes, followed by means of immediate measurement of the Cr(VI) concentration by inductively coupled plasma optical emission spectroscopy (700-ES, Varian, USA) at a wavelength of 267.716 nm. In this study, environmental temperature (5–50°C) was found hardly to affect the equilibrium adsorption amount of Cr(VI) and P(V) (data not shown).

Desorption experiments of QM-chitosan were conducted using 50-mL glass vials. The saturated QM-chitosan with Cr(VI) was separated by filtration and vacuum-dried at 80°C for 48 hr. Afterwards, 0.01 g of dried QM-chitosan with Cr(VI) and 40 mL of 1.5 mol/L NaCl solution were mixed in 50-mL glass vials, followed by shaking in an end-over-end manner at 26 r/min and at 25 ± 1°C for 12 hr (pre-experiments indicated that desorption would reach equilibrium within 12 hr). The suspensions with QM-chitosan were filtered and the Cr(VI) concentration was measured. The QM-chitosan on the filter was washed three times using deionized water and then vaccum-dried at 80°C for reuse. All batch experiments were run in duplicate.

Experimental procedures for P(V) adsorption and desorption were basically the same as those for Cr(VI). However, the concentration of P(V) was determined by the colorimetric method based on phosphomolybdenum blue reaction at a wavelength of 700 nm.

1.6. *Theoretical calculation method*

All the calculations were performed using GAUSSIAN 03 packages. The geometries were optimized at the B3LYP theory level. The single-point energy calculations were done at the B3LYP/6-311++g(2df,2p) level. For the solvation energy calculations, the polarizable continuum model method was used at the B3LYP/6-311++g(2df,2p) level with default at the UA0 radii.

2. Results and discussion

2.1. *Theoretical calculation*

Theoretical calculations show that the ΔG_m^0 (298 K) of reactions (2), (3) and (4) in the chitosan quaternization process

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(Fig. 1) was −72.64, 19.04 and 32.18 kJ/mol, respectively. According to the Van't hoff equations:

$$\Delta G_m = \Delta G_m{}^{\theta} + RT \ln\left(\frac{\prod_i \{\text{Product}\}^{\lambda_i}}{\prod_j \{\text{Reactant}\}^{\lambda_j}}\right) \quad (1)$$

where, ΔG_m is the *in situ* Gibbs energy of reaction, R (8.314 J/(mol/K)) is the gas constant, T (K) is the *in situ* temperature, λ_i is the stoichiometric coefficient of the species in the reaction i, and {} represents the activity of the chemical species.

The reaction is considered to be spontaneous when the $\Delta G_m^{\theta} < -41.80$ kJ/mol, while the reaction is considered to be impossible when the $\Delta G_m^{\theta} > 41.80$ kJ/mol (Lin, 2010). Thus, reaction (2) in Fig. 1 is considered to be spontaneous. In addition, reactions (3) and (4) can occur by changing the reaction conditions according to the calculated results. In this study, the temperature of the whole system was raised to decrease the ΔG_m and achieve the quaternization of chitosan (see Section 2.3).

2.2. Characterization of QM-chitosan and C-chitosan

The SEM-EDX analysis results of QM-chitosan and C-chitosan are shown in Appendix A Fig. S3. As observed, C and O are the main elements in the two kinds of chitosan (the occurrence of Pt resulted from the use of Pt during pre-treatment of the sample for SEM-EDX analysis). In addition, a small amount of Cl was found in C-chitosan, resulting from the residual epichlorohydrin after the chitosan monomer was crosslinked. Compared to C-chitosan, Fe was found in QM-chitosan, resulting from the addition of γ-Fe_2O_3. The content of Cl greatly increased in the QM-chitosan, which was considered to be the counter ion of quaternary ammonium in the QM-chitosan and indicated that the chitosan had been quaternized successfully. This inference was echoed by the zeta potential of QM-chitosan and C-chitosan. As shown in Fig. 2, the zeta potential of C-chitosan was negative in neutral and alkaline conditions. By contrast, the zeta potential of QM-chitosan remained positive throughout the pH range investigated, as a result of the quaternization of chitosan. As a consequence, anions (*e.g.*, Cr(VI), P(V)) can be easily adsorbed onto the QM-chitosan *via* electrostatic interaction.

Fig. 3 shows the FT-IR spectra of QM-chitosan, C-chitosan, QM-chitosan with Cr(VI), and P(V). Broad peaks around 1650 cm^{-1} and 1100 cm^{-1} were observed for all the samples and correspond to the bending vibration of the water molecules and the skeletal vibration of C–O (Zhang et al., 2007; Wen et al., 2011), respectively. For QM-chitosan, a broad peak occurred at 1500–1600 cm^{-1}, which was not found in the spectrum of C-chitosan and can be attributed to the C═N vibration (Adam et al., 2010). The occurrence of the C═N vibration peak indicated that the cyanuric chloride had been successfully grafted on the chitosan. After QM-chitosan adsorbed Cr(VI), a new peak occurred around 900 cm^{-1}, which was attributed to the vibration of Cr–O (Jia et al., 2012). After QM-chitosan adsorbed P(V), the peak corresponding to the P–O vibration occurred around 1000–1100 cm^{-1} (Gustafsson et al., 2008).

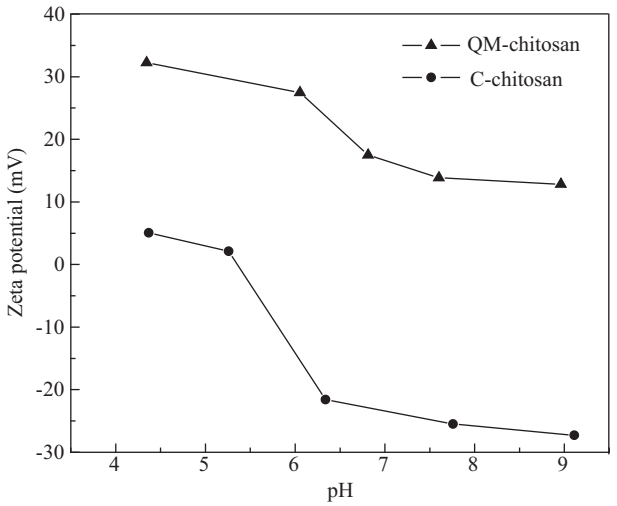

Fig. 2 – Zeta potentials of C-chitosan and QM-chitosan at different pH values.

2.3. Adsorption of Cr(VI) and P(V) on QM-chitosan

The adsorption kinetics of Cr(VI) and P(V) onto QM-chitosan are shown in Fig. 4. As observed, the adsorption of Cr(VI) reached equilibrium within 120 min, which is similar to the adsorption process of P(V). Rapid adsorption equilibrium can be mainly attributed to electrostatic interaction between the Cr(VI)/P(V) and the quaternary ammonium of chitosan. Linear and non-linear fittings of pseudofirst- and second-order models were used to describe the adsorption process of Cr(VI) and P(V) onto the QM-chitosan. The results showed that the adsorption kinetics of Cr(VI) and P(V) linearly fit the pseudosecond-order model best, with a reaction rate constant (*k*) of 0.087 and 0.13, respectively (Fig. 4).

The effects of pH on the adsorption of Cr(VI) and P(V) on QM-chitosan and C-chitosan are shown in Fig. 5. The adsorption capacity of QM-chitosan is significantly higher than that of C-chitosan, resulting from the role of quaternary ammonium on the QM-chitosan. With the increase of the solution pH, the

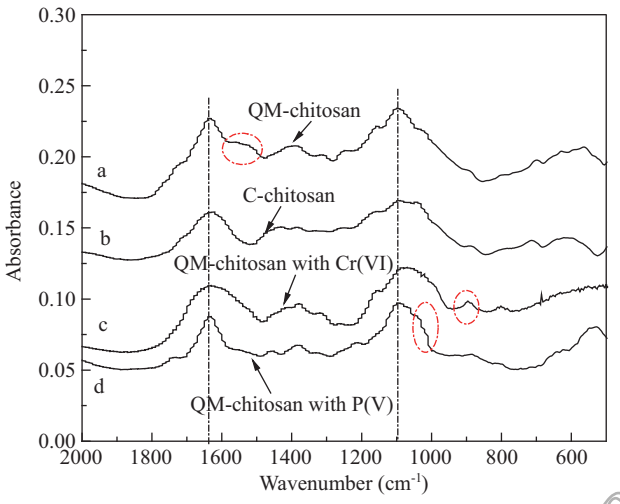

Fig. 3 – FT-IR spectra of chitosan.

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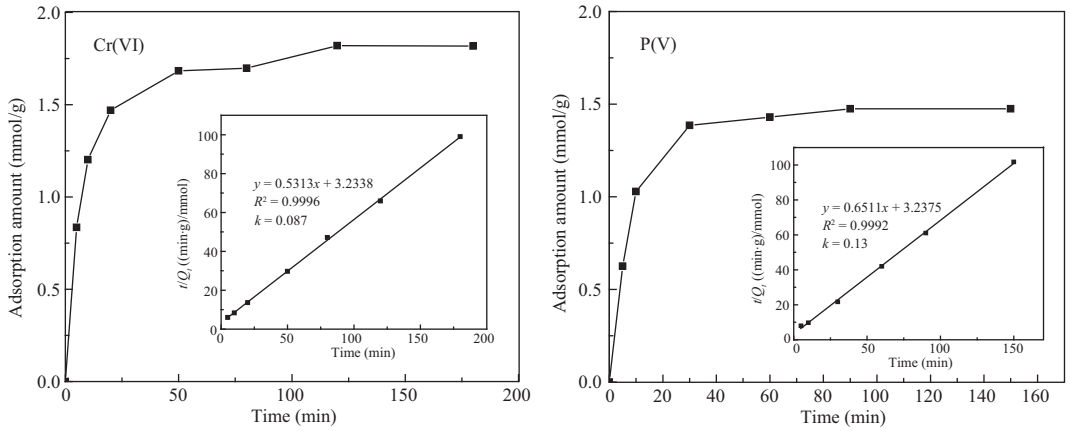

Fig. 4 – Adsorption kinetics of Cr(VI) and P(V) onto QM-chitosan. Experimental condition: initial concentrations of chromium(VI) and phosphorus(V) 1.0 and 0.65 mmol/L; pH 6.0 ± 0.2; QM-chitosan dosage 0.01 g; background electrolyte NaCl 5 mmol/L.

adsorption capacity of both QM-chitosan and C-chitosan decreased, which could be due to the following two aspects. On the one hand, the increasing pH promoted the deprotonation of Cr(VI) and P(V) (*e.g.*, $HCrO_4^- + OH^- = > CrO_4^{2-} + H_2O$; $H_2PO_4^- + OH^- = > HPO_4^{2-} + H_2O$; $HPO_4^{2-} + OH^- = > PO_4^{3-} + H_2O$). On the other hand, the rise of the solution pH also promoted the deprotonation of functional groups on QM-chitosan and C-chitosan (*e.g.*, the deprotonation of hydroxyl). These two factors are unfavorable for the electrostatic adsorption of Cr(VI) and P(V), thus resulting in a decrease of the adsorption amount with increasing solution pH. It is worth mentioning that C-chitosan barely adsorbed Cr(VI) and P(V) under a neutral and alkaline environment.

The effects of different anions (such as Cl^-, HCO_3^-, SO_4^{2-}) on the adsorption of Cr(VI) and P(V) by QM-chitosan are shown in Fig. 6. As observed, the adsorption of Cr(VI) was slightly inhibited in the presence of 10 mmol/L Cl^- or HCO_3^-, which could be attributed to the competition of Cl^- or HCO_3^- for adsorption sites on the QM-chitosan. However, the adsorption of P(V) on QM-chitosan was heavily inhibited by the co-present Cl^- or HCO_3^-, which indicated that the affinity of QM-chitosan with P(V) was relatively weak compared with Cr(VI). In the presence of 10 mmol/L SO_4^{2-}, the adsorption of Cr(VI) and P(V) was heavily inhibited, mainly due to the strong electrostatic interaction between QM-chitosan and SO_4^{2-} with two negative charges.

To further study the effect of ionic strength, the concentration of co-present NaCl was changed from 0 to 50 mmol/L (Appendix A Fig. S4). The results show that the inhibitory effect of NaCl increases with NaCl concentration, which confirms that the adsorption mechanisms of Cr(VI) and P(V) on the QM-chitosan are mainly by electrostatic interaction. In addition, the P(V) uptake was observed to decrease much greater than that of Cr(VI). In the presence of 50 mmol/L NaCl, the adsorption capacity of Cr(VI) on QM-chitosan was still as high as 1.154 mmol/g, while the adsorption capacity of P(V) was only 0.3 mmol/g. This interesting phenomena could result from the stronger affinity of QM-chitosan with Cr(VI) than that with P(V), which was echoed by the results of latter geometrical calculations and the Langmuir constant *b*.

Isothermality adsorption experiments were conducted and the results are shown in Fig. 7. The Langmuir and the Freundlich

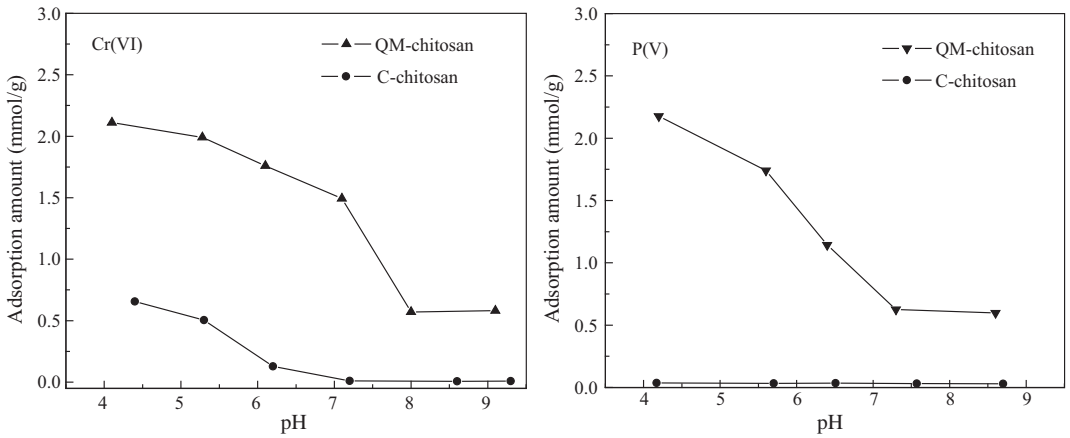

Fig. 5 – Effects of pH on the adsorption of Cr(VI) and P(V). Experimental condition: initial concentration of Cr(VI) and P(V) 1.0 and 0.65 mmol/L; adsorbent dosage 0.01 g; background electrolyte 5 mmol/L NaCl.

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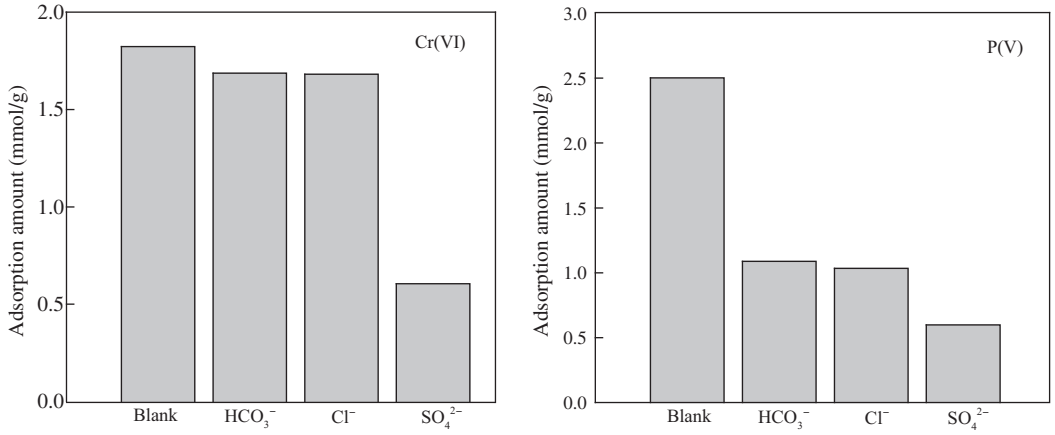

Fig. 6 – Effect of 10 mmol/L co-present anions on the adsorption of Cr(VI) and P(V) on QM-chitosan. Experimental condition: initial concentration of Cr(VI) and P(V) 1.0 mmol/L; QM-chitosan dosage 0.01 g; pH 6.0 ± 0.2.

models were applied in analyzing the isotherm adsorption of Cr(VI) and P(V). The two models can be expressed as Eqs. (2) and (3), respectively:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (2)$$

$$\mathrm{Log}Q_e = \frac{1}{n}\mathrm{Log}C_e + \mathrm{Log}K_f \quad (3)$$

where, C_e (mmol/L) is the equilibrium concentration of the adsorbate; Q_m (mmol/g) is the maximum adsorption capacity of the adsorbent; b (L/mmol) is a constant related to the adsorption energy; K_f is a constant related to the adsorption capacity of the adsorbent, and n is a constant related to the adsorption intensity.

The calculated constants and linear regression coefficient (R^2) for the Langmuir and Freundlich models are shown in Table 1.

Based on the regression correlation coefficients obtained, it is clear that the Langmuir model fitted the adsorption data of Cr(VI) and P(V) better than the Freundlich model, and indicated that the adsorption of Cr(VI) and P(V) onto QM-chitosan might occur in a homogeneous monolayer. Additionally, the b value of Cr(VI) adsorption (149.9) was much higher than that of P(V) adsorption (14.66), demonstrating a stronger affinity for Cr(VI) adsorption on the QM-chitosan (Auta and Hameed, 2014). The results of the geometrical calculations also echoed this interpretation. The interactions of $HCrO_4^-$/$H_2PO_4^-$ ions with QM-chitosan are presented in Fig. 8a and b. Given that the negative charges of $HCrO_4^-$/$H_2PO_4^-$ ions are dispersed among all the O atoms, the geometrical calculations show that the average N–O bond length between the QM-chitosan and $HCrO_4^-$ is 4.84 Å which is much smaller than that between QM-chitosan and $H_2PO_4^-$ (5.09 Å), indicating a stronger affinity between Cr(VI) and QM-chitosan.

However, the saturated adsorption amount (2.783 mmol/g) of P(V) was higher than that of Cr(VI) (2.323 mmol/g), which may be due to the smaller size of $H_2PO_4^-$ ions compared to $HCrO_4^-$ ions. The geometrical calculations of $HCrO_4^-$ and $H_2PO_4^-$ ions show that the average bond length of the Cr–O bond in $HCrO_4^-$ ions is larger than that of P–O bond in $H_2PO_4^-$ ions (Fig. 8c and d). The largest Cr–O bond length in $HCrO_4^-$ ions is 1.83 Å, which is also larger than the largest P–O bond length (1.68 Å) in $H_2PO_4^-$ ions. Furthermore, the atomic radius of Cr atom (140 pm) is larger than that of P atom (100 pm). Hence,

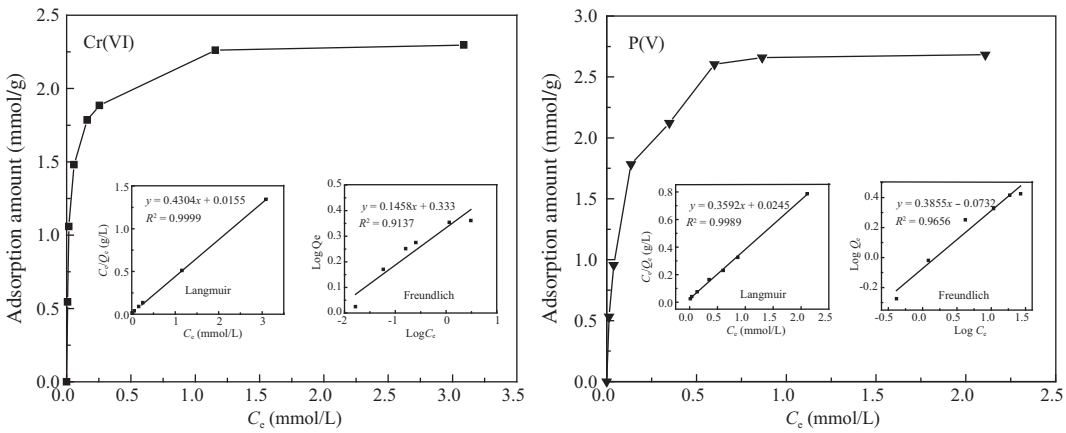

Fig. 7 – Adsorption isotherms of Cr(VI) and P(V) on QM-chitosan. Experimental condition: QM-chitosan dosage 0.01 g; pH 6.0 ± 0.2; background electrolyte 5 mmol/L NaCl.

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Table 1 – Langmuir and Freundlich constants for Cr(VI) and P(V) adsorption on QM-chitosan.

	Langmuir isotherm			Freundlich isotherm		
	b	Q_m (mmol/g)	R^2	n	K_f	R^2
Cr(VI)	149.9	2.323	0.9999	6.859	2.154	0.9173
P (V)	14.66	2.783	0.9989	2.594	0.845	0.9656

the volume of $HCrO_4^-$ ions is obviously bigger than that of $H_2PO_4^-$ ions considering that both ions have a tetrahedral structure, leading to the saturated adsorption amount of P(V) being higher than for Cr(VI).

2.4. Desorption and regeneration

The reusability of adsorbents is of great importance as a cost-effective process in water treatment. For the environmental sustainability of an adsorbent, a high regeneration capacity would add much value in water treatment. In this study, NaCl solution was chosen as the regeneration agent. Pre-experiments showed that the desorption efficiency of Cr(VI) and P(V) increased with the increase of NaCl concentration. However, a high NaCl concentration would obviously result in a higher cost. In view of the above, 1.5 mol/L of NaCl solution was selected to regenerate QM-chitosan. Four cycles of adsorption–desorption studies were accordingly carried out. The results showed that QM-chitosan still had a high regeneration capacity after four adsorption–desorption cycles (Appendix A Fig. S5). Furthermore, a higher recovery ratio was observed for QM-chitosan with P(V) compared to that with Cr(VI), possibly resulting from the stronger affinity of Cr(VI) with QM-chitosan.

3. Conclusions

A quaternization pathway based on theoretical calculations has been achieved successfully and a new chitosan derivative with quaternary ammonium and magnetic property (QM-chitosan) has been prepared. The QM-chitosan was characterized with FT-IR, TGA, SEM-EDX and zeta potential, and was used for the removal of Cr(VI) and P(V) from aqueous environments. The results of batch experiments demonstrated that QM-chitosan can effectively remove Cr(VI) and P(V) from aqueous environments. Both adsorption kinetics were found to be well described by a pseudosecond-order equation and the main mechanism was believed to be electrostatic interaction. The adsorption isotherms of both Cr(VI) and P(V) on the QM-chitosan can be well described by the Langmuir model. The saturated adsorption amount of P(V) (2.783 mmol/g) was found to be higher than that of Cr(VI) (2.323 mmol/g). However, the QM-chitosan had a stronger affinity with Cr(VI) than that with P(V), according to theoretical calculation and experimental results. In addition, the high regeneration capacity of QM-chitosan was achieved through the adsorption–desorption evaluation.

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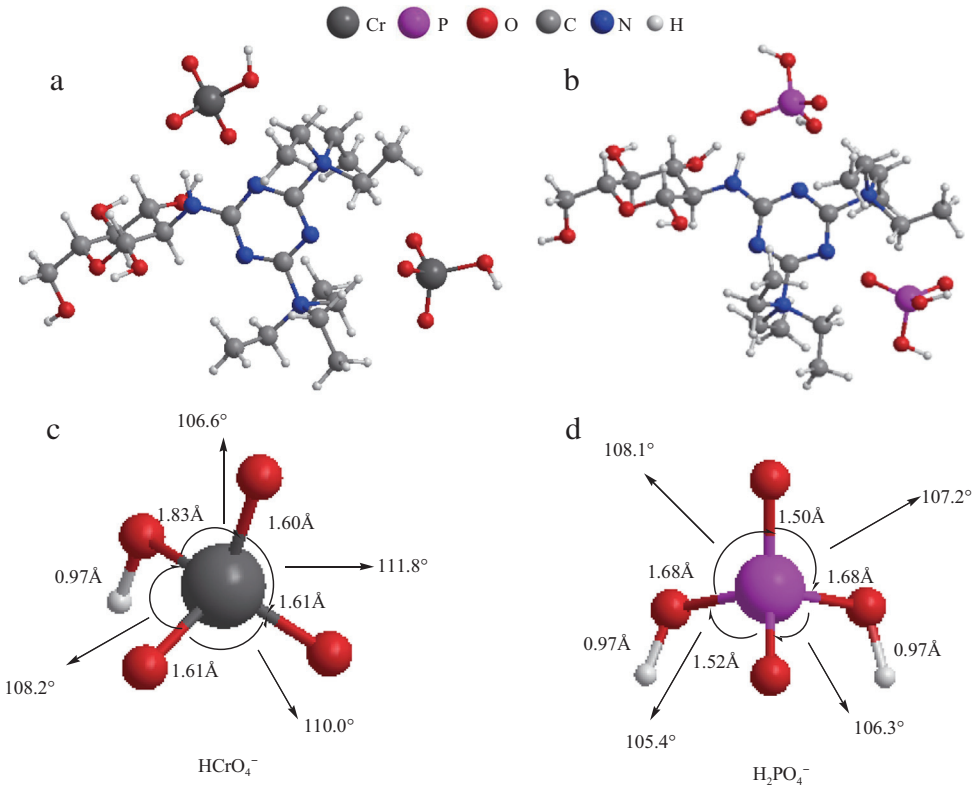

Fig. 8 – Interactions between QM-chitosan and $HCrO_4^-$ ions (a)/$H_2PO_4^-$ ions (b), and the geometries of $HCrO_4^-$ (c) and $H_2PO_4^-$ (d).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in online version at http://dx.doi.org/10.1016/j.jes.2014.03.005.

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