Highly efficient removal of chromium(VI) from aqueous solution using polyaniline/sepiolite nanofibers

Jun Chen, Xiaoqin Hong, Qingdong Xie, Diankai Li and Qianfeng Zhang

ABSTRACT

Polyaniline/sepiolite (PANI/sepiolite) nanofibers were prepared by *in situ* chemical oxidation polymerization in the presence of sepiolite. The effect of aniline/sepiolite weight ratio on the nanostructure of PANI/sepiolite composites was investigated by field-emission scanning electron microscopy. The adsorption of Cr(VI) onto the PANI/sepiolite nanofibers was highly dependent on pH values. The pseudo-second-order and Langmuir isothermal models can well describe the adsorption kinetics and adsorption isotherm, respectively. The maximum adsorption capacity of the PANI/sepiolite nanofibers for Cr(VI) was up to 206.6 mg/g at 25 °C and increased with the increase in temperature. Desorption experiments indicated that PANI/sepiolite can be regenerated and reused for two consecutive cycles with no loss of its removal efficiency. PANI/sepiolite nanofibers can be used as a highly efficient and economically viable adsorbent for Cr(VI) removal due to their excellent adsorption characteristics.

Key words | adsorption, hexavalent chromium, kinetics, nanofibers, polyaniline/sepiolite, regeneration

Jun Chen (corresponding author)
Xiaoqin Hong
Qingdong Xie
Qianfeng Zhang
School of Chemistry and Chemical Engineering,
Institute of Molecular Engineering & Applied Chemistry, Anhui University of Technology,
Ma'anshan 243002,
China
E-mail: *junchen@ahut.edu.cn*

Diankai Li
School of Materials Science and Engineering,
Anhui University of Technology,
Ma'anshan 243002,
China

INTRODUCTION

Due to increased concern about the global environmental pollution problem, more and more researchers have dedicated their efforts to finding available approaches to deal with heavy metal ions. Among those various kinds of heavy metal ions, the Cr(VI) ion is one of the most toxic pollutants due to toxicity, carcinogenicity and mutagenicity. To date, many approaches including adsorption (Duranoğlu *et al.* 2012), chemical precipitation (Esmaeili *et al.* 2005), ion exchange (Shi *et al.* 2009) and membrane filtration (Kozlowski & Walkowiak 2002) have been developed to reduce/remove Cr(VI) ions from aqueous solutions. Among these approaches, adsorption is an easy-to-operate and cost-effective process for the removal of Cr(VI) from water and hence has attracted attention in recent years (Fu & Wang 2011).

Different types of adsorbent materials have been widely studied for the removal of Cr(VI) from water including activated carbons (Duranoğlu *et al.* 2012), clay minerals (Bhattacharyya & Gupta 2006) and organic resin (Misra *et al.* 2011). However, conventional adsorbents often show a limited adsorption capacity or no reduction ability because they do not have enough surface area, functional groups or hydrophilic surface. Polyaniline has shown its good potential for removing heavy metal ions because it carries large amounts of amine and imine functional groups which can chelate metal ions and can also adsorb anionic metal species through electrostatic or hydrogen bonding (Krishnani *et al.* 2013). Polyaniline doped with sulfuric acid has been used to remove Cr(VI) from aqueous solution. Adsorption equilibrium was attained within a short contact time of 1.5 h and the maximum adsorption capacity of Cr(VI) was 95.79 mg/g (Zhang *et al.* 2010). Bulk-quantity one-dimensional polyaniline nanowire/tubes with rough surfaces have been prepared by a simple chemical oxidation method and used for removal of Cr(VI) in aqueous solution. This kind of polyaniline (PANI) nanostructure can not only remove Cr(VI) rapidly and effectively but also be easily regenerated for reuse (Guo *et al.* 2011). Polyaniline (PANI) nanoparticles and 1D nanostructures have been prepared by a facile sono-assisted chemical oxidation method in protonic acids like HCl, surfulamic acid, citric acid, taurine and neutral deionized

doi: 10.2166/wst.2014.361

water for removal of aqueous Cr(VI). Their adsorption efficiencies varied depending on the protonic acids and the consequent molecular structures of PANIs (Wang *et al.* 2014). However, bare PANI particles are easily aggregated in aqueous solutions, which results in low adsorption capacity and slow kinetics. In order to avoid aggregation of PANI properly and enhance the adsorption capacity, PANI composites have been subject to extensive studies by *in situ* polymerization of aniline in the presence of other materials. Core–shell polyaniline/polystyrene nanocomposite was synthesized and used for removal of Cr(VI) from aqueous solutions. The optimum conditions for Cr(VI) removal were achieved with pH 4, adsorbent dosage of 15 g L^{-1}, and 30 min equilibrium time (Lashkenari *et al.* 2012). Humic acid has been used to composite with polyaniline, which played an important role in modifying the morphology, preventing the aggregation of PANI, and improving the uptake properties of Cr(VI) on the composite in pH 3.0–7.0 (Li *et al.* 2011). Dodecylbenzene-sulfonic-acid doped polyaniline/multi-walled carbon nanotube (DP/MWCNT) nanocomposite has been found to be an ideal adsorbent for the removal of Cr(VI) as compared to pristine and oxidized MWCNTs (Kumar *et al.* 2013). Polyacrylonitrile/polyaniline core–shell nanofibers have been prepared via electrospinning followed by *in situ* polymerization of aniline and exhibited excellent adsorption capability when used as an absorbent for Cr(VI) ions (Wang *et al.* 2013). Polyaniline/natural fiber composite adsorbents have also been developed for Cr(VI) removal (Kumar & Chakraborty 2009; Zheng *et al.* 2012). Two-dimensional nanomaterials, such as montmorillonite and graphene oxide, have also been used as the scaffold to prepare polyaniline composite adsorbents for Cr(VI) removal (Chen *et al.* 2013; Zhang *et al.* 2013).

Sepiolite is a naturally occurring fibrous phyllosilicate with a large specific surface area (more than 200 m^2/g). Because of its natural abundance, the dimensions of the isolated fiber, and the silanol-based chemistry of the surface, sepiolite shows excellent adsorption efficiency for heavy metal ions (Doğan *et al.* 2008; Liang *et al.* 2011). In this paper, we report on a facile synthetic method at room temperature and application of PANI/sepiolite nanofibers for the removal of Cr(VI) from aqueous solution. Sepiolite can be used as template to orient the growth of PANI nanofibers and the resulting PANI/sepiolite nanofibers exhibit high efficiency for Cr(VI) removal. The effect of several parameters, namely pH, contact time, temperature, initial concentration of Cr(VI) and dose of adsorbent, were tested in batch mode.

MATERIALS AND METHODS

Materials

Aniline monomer was purchased from Sinopharm Chemical Reagent Co., Ltd (China) and stored at −4 °C prior to use. Ammonium persulfate (APS), 1,5-diphenylcarbohydrazide, potassium dichromate, sodium hydroxide, sulfuric acid and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and used without further treatment. Sepiolite (Pangel S9) was purchased from TOLSA, S.A. (Spain).

Preparation of PANI/sepiolite nanofibers

PANI/sepiolite nanofibers were prepared by an *in situ* chemical oxidation method. First, 0.8 g aniline monomer was added to 160 mL of aqueous solution containing 0.4 g sepiolite and 0.5 mol hydrochloric acid and then stirred for 30 min. The polymerization was started by the introduction of APS solution (1.96 g APS in 40 mL of 0.5 mol/L hydrochloric acid) dropwise. An overnight reaction was allowed to ensure completion of polymerization. The resultant precipitate was filtered and sequentially washed with copious amounts of 0.1 mol/L hydrochloric acid and industrial alcohol until the filtrate was clear. Finally, the product was dried at 50 °C in an oven. PANI/sepiolite nanofibers with different sepiolite/aniline weight ratios were prepared according to the aforementioned method.

Adsorption studies

Potassium dichromate was dissolved in deionized water to give an aqueous stock solution of Cr(VI) (1,000 mg/L). Aqueous Cr(VI) solutions with different concentrations were obtained by diluting the stock solution with deionized water. The concentration of Cr(VI) was analyzed by spectrophotometer (UV3600, Shimadzu Corporation) using 1,5-diphenylcarbazide as the complexing agent at a wavelength of 540 nm (GB 7467-87) (Zhang *et al.* 2010).

To investigate the effect of pH on the removal of Cr(VI), adsorption studies were performed by varying the pH of the Cr(VI) solution from 2.0 to 10.0. The pH values of the Cr(VI) solution were adjusted by NaOH and HCl. After 3 h of contact the solution was centrifuged, and the Cr(VI) solution after adsorption was analyzed for residual Cr(VI). The Cr(VI) removal efficiency was

determined using Equation (1):

$$\% \text{ removal} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of Cr(VI), respectively.

For the kinetics study, 250 mg of PANI/sepiolite nanofibers was dispersed in 250 mL of Cr(VI) solution at pH 2 and placed in a thermostatic shaker with agitation at 200 rpm. An appropriate amount of the solution was taken out at predetermined intervals and centrifuged quickly. The Cr(VI) solutions after adsorption were used for analyzing Cr(VI) concentration. The adsorption capacity of the PANI/sepiolite q_t (mg/g) at time t was obtained from Equation (2):

$$q_t = \left(\frac{C_0 - C_t}{m}\right) V \quad (2)$$

where m is the adsorbent mass (g) and V is the volume of solution (L), and C_t is the concentration of Cr(VI) at any time t (mg/L).

The adsorption isotherm at three different temperatures (25, 35, 45 °C) was studied with different initial Cr(VI) concentrations ranging from 100 to 300 mg/L at pH 2 while maintaining the PANI/sepiolite dose of 1 g/L and contact time of 6 h. The amount of Cr(VI) adsorbed was calculated using Equation (3):

$$q_e = \left(\frac{C_0 - C_e}{m}\right) V \quad (3)$$

where q_e is the equilibrium adsorption capacity (mg/g).

All the adsorption experiments are repeatable and three replicates were conducted.

Regeneration study

For desorption studies, 0.05 g of PANI/sepiolite nanofibers was first contacted with 50 mL of 100 mg/L Cr(VI) at pH 2 for 6 h. Desorption of Cr(VI)-loaded PANI/sepiolite nanofibers was performed by using 50 mL of 0.1 M NaOH solution. Thereafter, for regeneration of the sorption sites of the adsorbent, PANI/sepiolite nanofibers were contacted

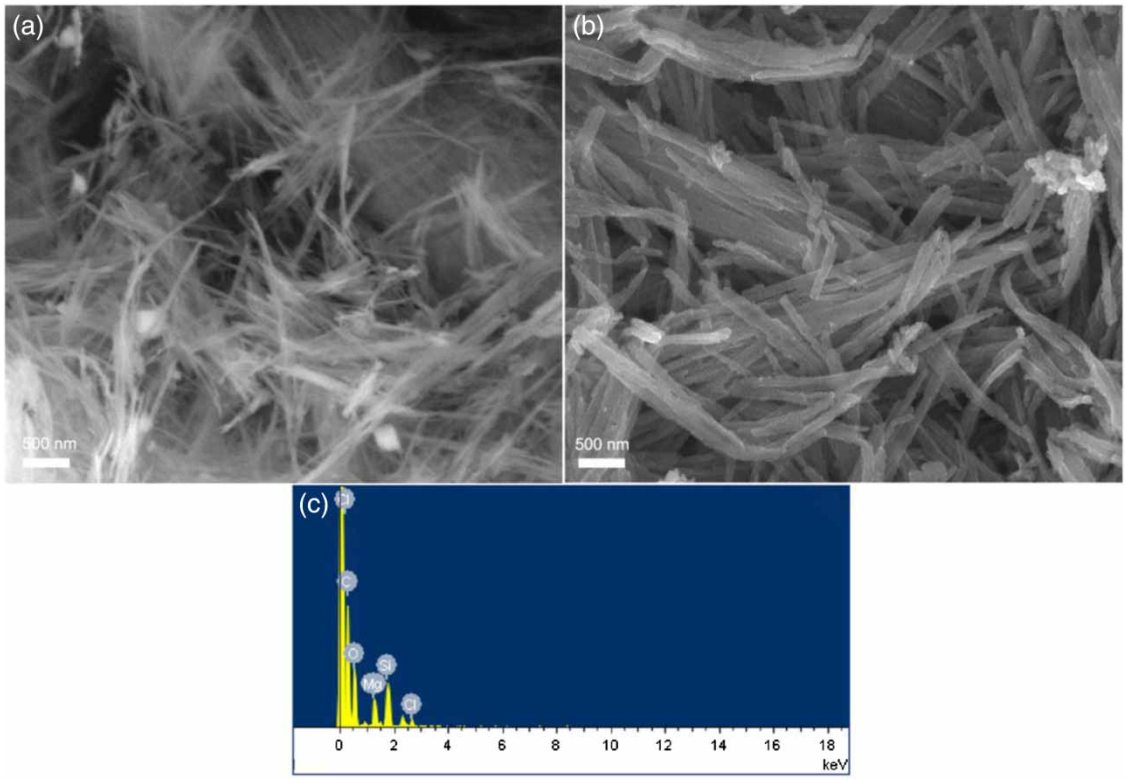

Figure 1 | (a) SEM image of sepiolite; (b) SEM and (c) EDX images of PANI/sepiolite.

with 2 M HCl solution. Four consecutive adsorption–desorption cycles were examined for the regenerated PANI/sepiolite nanofibers to study the reusability of PANI/sepiolite nanofibers.

Morphology and composition studies

The morphology and distribution of the elemental components of PANI/sepiolite nanofibers were characterized by scanning electron microscopy (SEM) equipped with the energy dispersive analysis system of an X-ray spectrometer (EDX) (Nova NanoSEM 430, FEI Company).

RESULTS AND DISCUSSION

Characterization of PANI/sepiolite

SEM was used to characterize the morphology of sepiolite and PANI/sepiolite (shown in Figures 1(a) and 1(b)). It is observed that sepiolite fibers are 1–2 μm in length and 20–30 nm in diameter. PANI/sepiolite was prepared by *in situ* polymerization and presented a fibrous structure. The diameter of PANI/sepiolite in the range of 100–150 nm is larger than that of sepiolite, which indicates that PANI grew on the fibrous surface of sepiolite during the polymerization process. The main elemental compositions of PANI/sepiolite composite were characterized by EDX analysis (shown in Figure 1(c)). The existence of C, O, Cl, Si and Mg is verified, suggesting it is a composite of PANI and sepiolite.

Effect of pH

The effect of pH on the adsorption of Cr(VI) was studied and results are presented in Figure 2. It can be seen that the removal efficiency for Cr(VI) decreased with the increase of pH values from 2 to 10. It is well known that Cr(VI) in aqueous solutions mostly exists in the form of $HCrO_4^-$ or CrO_4^{2-} ions at lower pH (2–6). In the case of PANI adsorbent, it has been reported that the adsorption process occurred via the ion exchange property of PANI by replacing the doped Cl^{-1} ions with

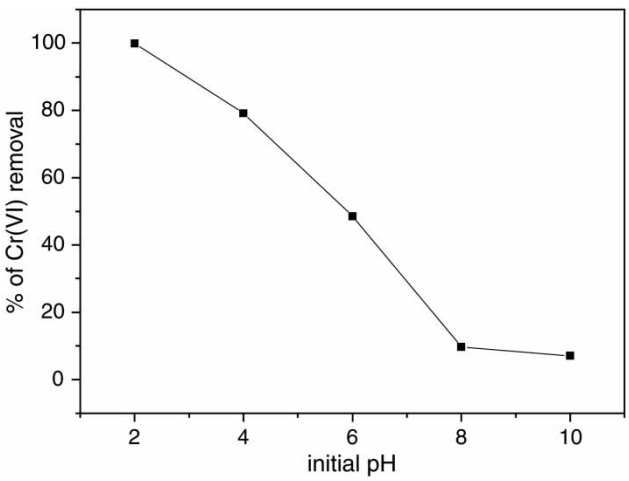

Figure 2 | Effect of pH on the adsorption of Cr(VI) by PANI/sepiolite nanofibers (PANI/sepiolite dose 1 g/L; initial Cr(VI) 200 ppm; time 3 h).

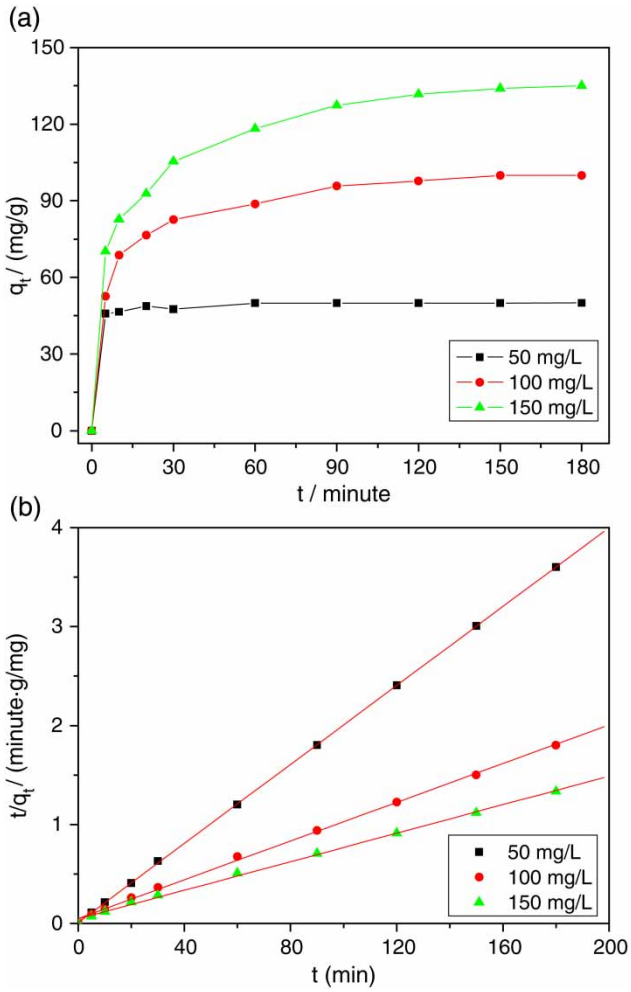

Figure 3 | (a) Adsorption kinetic curves and (b) pseudo-second-order kinetic plots for the adsorption of Cr(VI) at different initial concentrations.

Table 1 | Kinetic parameters for Cr(VI) adsorption onto PANI/sepiolite nanofibers

C_0 (mg/L)	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min)	R^2
50	50.00	50.15	0.034	0.999
100	99.92	102.25	0.0019	0.999
150	135.00	138.89	0.0011	0.999

$HCrO_4^-$ or CrO_4^{2-} ions (Krishnani *et al.* 2013). The amount of OH^{-1} ions increased with the increase in pH values, which resulted in the decrease of removal efficiency for the competitive interaction between the OH^{-1} ions and $HCrO_4^-$ or CrO_4^{2-} ions on the adsorbent sites. Based on these observations, all further adsorption experiments were performed at pH 2.

Adsorption kinetics

To determine the optimum adsorption time, adsorption kinetic experiments were conducted at different initial concentrations of Cr(VI). The results are shown in Figure 3. The rapid removal is due to the uniform and easily accessible surface sites on the PANI/sepiolite nanofibers. In order to understand better the adsorption behaviour, a pseudo-second-order model was applied to fit the adsorption experimental data:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the rate constant (g mg^{-1} min). The results (seen in Figure 3(b)) show that t/q_t *versus* t is linear for PANI/

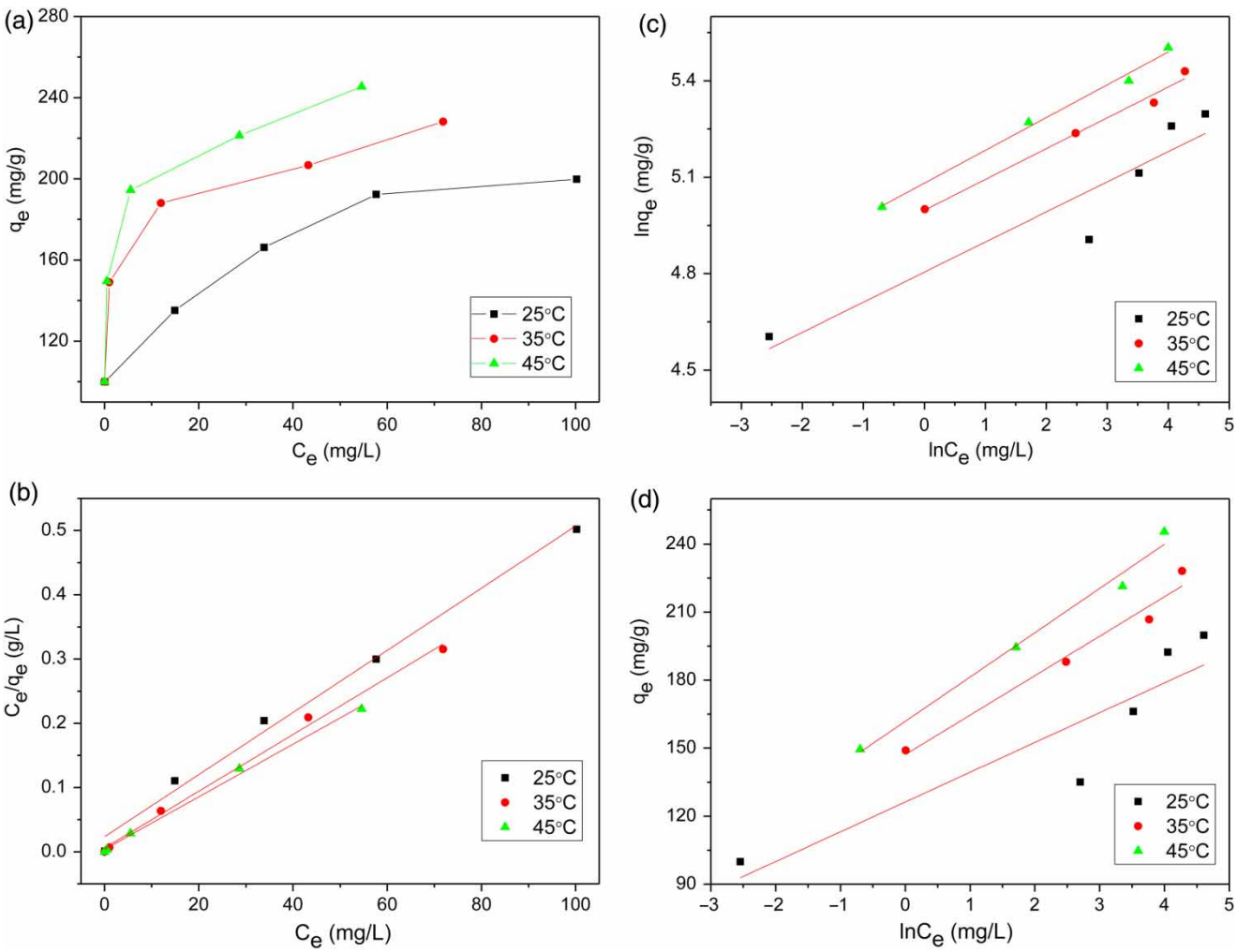

Figure 4 | (a) The plot of adsorption capacity against equilibrium concentration of Cr(VI); (b) Langmuir adsorption isotherm, (c) Freundlich adsorption isotherm, and (d) Temkin isotherm for Cr(VI) ion adsorption on PANI/sepiolite nanofibers.

Table 2 | Parameters of the Langmuir, Freundlich, and Temkin isotherm models

	Langmuir constants			Freundlich constants			Temkin constants		
Temperature (°C)	q_m (mg/g)	b (L/mg)	R^2	k_F (mg/g)	n	R^2	A (L/g)	B (kJ/mol)	R^2
25	206.61	0.21	0.990	122.08	10.68	0.860	126.24	13.12	0.780
35	226.24	0.77	0.995	147.97	10.43	0.982	147.17	17.40	0.961
45	244.50	1.12	0.996	161.03	9.80	0.989	161.83	19.52	0.980

sepiolite at different initial Cr(VI) concentrations. Values of k_2, k_2 and the correlation coefficient R^2 are calculated and listed in Table 1. It is observed that the correlation coefficient R^2 for the pseudo-second-order kinetic model is above 0.999 and the calculated values of q_e for the pseudo-second-order kinetic model are in good agreement with the experimental values of q_e, indicating that the adsorption kinetics accord well with the pseudo-second-order model.

Adsorption isotherm

Adsorption isotherms were studied at three different temperatures (25, 35 and 45 °C) and are shown in Figure 4(a). The adsorption capacity of polyaniline/sepiolite nanofibers increases with increase in temperature, which indicates that the adsorption process is endothermic. Langmuir, Freundlich and Temkin isotherm models were extensively used to investigate the isotherm data. The three linear isotherm equations are expressed as the following:

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{C_e}{q_m b} + \frac{C_e}{q_m} \tag{5}$$

$$\text{Freundlich: } \ln q_e = \ln k_F + \frac{1}{n}\ln C_e \tag{6}$$

$$\text{Temkin: } q_e = A + B \ln C_e \tag{7}$$

where q_m and b are the Langmuir constants related to the adsorption capacity (mg g^{-1}) and the rate of adsorption (L mg^{-1}), respectively; k_F and n are the Freundlich isotherm parameters related to adsorption capacity (mg g^{-1}) and intensity of adsorption, respectively; A and B are the Temkin isotherm constants. The linearized Langmuir, Freundlich and Temkin isotherms for the three different temperatures are shown in Figures 4(b)–4(d). Table 2 summarizes the Langmuir, Freundlich and Temkin isotherm parameters calculated from the intercept and slope of the linear equations. The Langmuir model fitted well to the isotherm data compared to the other two models due to the higher values of the correlation coefficient, which indicated a monolayer adsorption for the uptake of Cr(VI) on the surface of the PANI/sepiolite nanofibers. The maximum adsorption capacity increased from 206.6 to 244.5 mg/g with an increase in temperature from 25 to 45 °C.

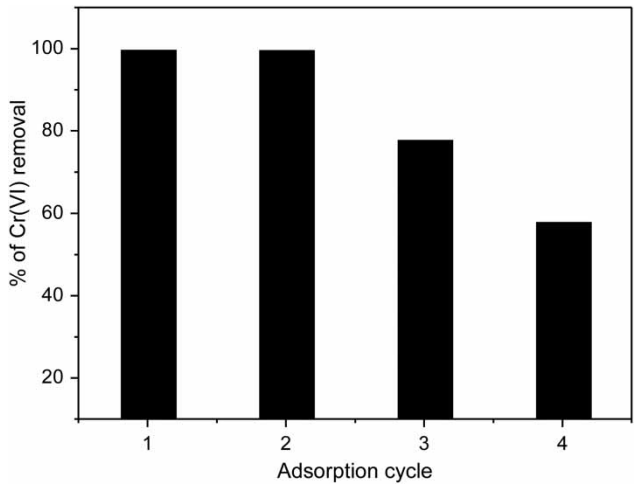

Figure 5 | Regeneration of PANI/sepiolite for four cycles.

Regeneration studies

Regeneration of PANI/sepiolite nanofibers was studied by performing an adsorption–desorption experiment for four consecutive cycles. Only 6.93% of the adsorbed Cr(VI) was desorbed in the first cycle of desorption. A lower desorption efficiency has also been observed for polyaniline nanowire/tubes (Guo *et al.* 2011) and kapok/PANI nanofibers (Zheng *et al.* 2012). This is due to the reduction of adsorbed Cr(VI) to Cr(III) should be treated as a single unit, not divided by PANI which could not be desorbed upon treatment with NaOH solution (Guo *et al.* 2011; Zheng *et al.* 2012). Figure 5 shows the removal efficiency for Cr(VI) of PANI/sepiolite nanofibers in each cycle of adsorption. It is observed that the removal efficiency

(100%) of PANI/sepiolite nanofibers remained almost the same for the first two cycles, and in the subsequent third (78.1%) and fourth cycles (58.1%) there is a gradual decrease in removal efficiency. Therefore, the PANI/sepiolite nanofibers can be successfully reused for the two adsorption cycles with no loss of removal efficiency.

CONCLUSIONS

Sepiolite is a natural resource and has a fibrous structure with a large specific surface area. Due to its unique structure, environmental friendliness and cost effectiveness, this raw material is combined with PANI by *in situ* polymerization to obtain a novel adsorbent for efficient Cr(VI) removal from aqueous solution. Sepiolite served as a template to guide the growth of PANI/sepiolite nanofibers during the polymerization process. When the as-synthesized PANI/sepiolite nanofibers were used as absorbents for Cr(VI) removal from aqueous solution, the PANI/sepiolite nanofibers exhibited the highest removal efficiency for Cr(VI) at pH 2. The adsorption kinetics and isotherms were well described by pseudo-second-order and Langmuir models, respectively. The maximum adsorption capacity increased with the increase in temperature. PANI/sepiolite nanofiber adsorbent can be regenerated and reused for two consecutive cycles with no loss of removal efficiency. Therefore PANI/sepiolite nanofibers could be a useful adsorbent for treatment of water contaminated with Cr(VI).

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 21207001), the Natural Science Fund of Anhui Provincial Education Committee of P. R. China (KJ2012Z036), the Anhui Province College Outstanding Young Talent Fund of P. R. China (2012SQRL032ZD) and the National Undergraduate Training Programs for Innovation and Entrepreneurship (201310360026).

REFERENCES

Bhattacharyya, K. G. & Gupta, S. S. 2006 Adsorption of chromium (VI) from water by clays. *Industrial & Engineering Chemistry Research* **45** (21), 7232–7240.

Chen, J., Hong, X., Zhao, Y., Xia, Y., Li, D. & Zhang, Q. 2013 Preparation of flake-like polyaniline/montmorillonite nanocomposites and their application for removal of Cr(VI) ions in aqueous solution. *Journal of Materials Science* **48** (21), 7708–7717.

Doğan, M., Turhan, Y., Alkan, M., Namli, H., Turan, P. & Demirbaş, Ö. 2008 Functionalized sepiolite for heavy metal ions adsorption. *Desalination* **230** (1–3), 248–268.

Duranoğlu, D., Trochimczuk, A. W. & Beker, U. 2012 Kinetics and thermodynamics of hexavalent chromium adsorption onto activated carbon derived from acrylonitrile-divinylbenzene copolymer. *Chemical Engineering Journal* **187**, 193–202.

Esmaeili, A., Mesdaghi Nia, A. & Vazirinejad, R. 2005 Chromium (III) removal and recovery from tannery wastewater by precipitation process. *American Journal of Applied Sciences* **2** (10), 1471–1473.

Fu, F. & Wang, Q. 2011 Removal of heavy metal ions from wastewaters: a review. *Journal of Environmental Management* **92** (3), 407–418.

Guo, X., Fei, G. T., Su, H. & Zhang, L. D. 2011 High-performance and reproducible polyaniline nanowire/tubes for removal of Cr(VI) in aqueous solution. *The Journal of Physical Chemistry C* **115** (5), 1608–1613.

Kozlowski, C. A. & Walkowiak, W. 2002 Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes. *Water Research* **36** (19), 4870–4876.

Krishnani, K. K., Srinives, S., Mohapatra, B. C., Boddu, V. M., Hao, J., Meng, X. & Mulchandani, A. 2013 Hexavalent chromium removal mechanism using conducting polymers. *Journal of Hazardous Materials* **252**, 99–106.

Kumar, P. A. & Chakraborty, S. 2009 Fixed-bed column study for hexavalent chromium removal and recovery by short-chain polyaniline synthesized on jute fiber. *Journal of Hazardous Materials* **162** (2–3), 1086–1098.

Kumar, R., Ansari, M. O. & Barakat, M. A. 2013 DBSA doped polyaniline/multi-walled carbon nanotubes composite for high efficiency removal of Cr(VI) from aqueous solution. *Chemical Engineering Journal* **228**, 748–755.

Lashkenari, M. S., Davodi, B., Ghorbani, M. & Eisazadeh, H. 2012 Use of core-shell polyaniline/polystyrene nanocomposite for removal of Cr(VI). *High Performance Polymers* **24** (5), 345–355.

Li, Q., Sun, L., Zhang, Y., Qian, Y. & Zhai, J. 2011 Characteristics of equilibrium, kinetics studies for adsorption of Hg(II) and Cr(VI) by polyaniline/humic acid composite. *Desalination* **266** (1), 188–194.

Liang, X., Xu, Y., Sun, G., Wang, L., Sun, Y., Sun, Y. & Qin, X. 2011 Preparation and characterization of mercapto functionalized sepiolite and their application for sorption of lead and cadmium. *Chemical Engineering Journal* **174** (1), 436–444.

Misra, R. K., Jain, S. K. & Khatri, P. K. 2011 Iminodiacetic acid functionalized cation exchange resin for adsorptive removal of Cr(VI), Cd(II), Ni(II) and Pb(II) from their aqueous solutions. *Journal of Hazardous Materials* **185** (2), 1508–1512.

Shi, T., Wang, Z., Liu, Y., Jia, S. & Changming, D. 2009 Removal of hexavalent chromium from aqueous solutions by D301, D314

and D354 anion-exchange resins. *Journal of Hazardous Materials* **161** (2), 900–906.

Wang, J., Pan, K., Giannelis, E. P. & Cao, B. 2013 Polyacrylonitrile/polyaniline core/shell nanofiber mat for removal of hexavalent chromium from aqueous solution: mechanism and applications. *RSC Advances* **3** (23), 8978–8987.

Wang, J., Zhang, K. & Zhao, L. 2014 Sono-assisted synthesis of nanostructured polyaniline for adsorption of aqueous Cr(VI): effect of protonic acids. *Chemical Engineering Journal* **239**, 123–131.

Zhang, R., Ma, H. & Wang, B. 2010 Removal of chromium (VI) from aqueous solutions using polyaniline doped with sulfuric acid. *Industrial & Engineering Chemistry Research* **49** (20), 9998–10004.

Zhang, S., Zeng, M., Xu, W., Li, J., Li, J., Xu, J. & Wang, X. 2013 Polyaniline nanorods dotted on graphene oxide nanosheets as a novel super adsorbent for Cr(VI). *Dalton Transactions* **42** (22), 7854–7858.

Zheng, Y., Wang, W., Huang, D. & Wang, A. 2012 Kapok fiber oriented-polyaniline nanofibers for efficient Cr(VI) removal. *Chemical Engineering Journal* **191**, 154–161.

First received 8 June 2014; accepted in revised form 6 August 2014. Available online 21 August 2014