Removal of Arsenic in Water by an Ion-Exchange Fiber with Amino Groups

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ABSTRACT: A new type of ion-exchange fiber with amino groups, called RPFA-I, was prepared. The amino modification and stretching resistance of RPFA-I were characterized by FTIR spectrum, SEM test, and auto-tensile test, respectively, and the removal of arsenite and arsenate in solution by RPFA-I was investigated. The obtained experimental results show that RPFA-I fibers have fine mechanical properties, and the amino functional groups have grafted to the surface of the matrix material. The adsorption results show that RPFA-I has a high capacity and good adsorption kinetic property in removal of arsenate and arsenite at the trace level. The removal efficiency was 70% for arsenite and 93% arsenate, respectively, at the concentration of 5 mg/L. The isothermal adsorptions were correspondent to Langmiur/Frundlich adsorption equation, and the adsorption kinetics was fit to the Lagergren pseudosecond order rate equation. The adsorption of the used adsorbent could be efficiently regenerated by 0.1M NaOH in a simple way. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3934–3940, 2008

Key words: Fibrous ion exchange fiber; arsenite; arsenate; adsorption; arsenic removal

INTRODUCTION

Arsenic is ubiquitous in the atmosphere, soils and rocks, natural waters, and organisms. Arsenic concentration found in natural waters is ranging from less than 0.5 mg/L to more than 5000 mg/L,[1] but in fresh water it is required to be lower than 10 μg/L to avoid the toxicity.[2] Arsenic has been legalized to be the cancer evocator by WHO (Worldwide Health Organization).[3–5] But more than 70 countries are still disturbed by arsenic contamination.[6] Because of this high risk, Contamination of potable ground water with arsenic and its removal in water have become the focuses of increasing attention worldwide. Adsorption and ion exchange are more effective treatment methods adopted by many researchers. The popular adsorbents are usually activated carbon,[7] activated alumina,[8] ferreous oxidation,[9] biological adsorbents,[10] ion-exchange resin,[11] and ion-exchange fiber.[12] But not all of these materials are efficiently useful for aqueous arsenic removal. For example, granular resin has been successfully used in many fields especially in water treatment, but it

also has some disadvantages such as the poor kinetic property.

In comparison with the traditional adsorbents, fibrous material has many unique advantages: (1) larger specific surface area and smaller diameter; (2) better elasticity; (3) fibrous material can be made in the form of filaments, staple fibers, nonwoven fabrics, threads and other textile items; (4) the material can be regenerated and reused for many cycles.[13]

So it is meaningful to select proper matrix material to synthesize functional fibrous material.

And this article is aimed to search for a new fibrous material for aqueous arsenic removal. There have been numerous researches on the adsorption of arsenic from water by fibrous materials.[12,14] Nevertheless, although they have exhibited good adsorption capacity for arsenic uptake, modification process may be further required for adsorption application, because the defects such as poor mechanical properties and the difficulty in regeneration, restrict the materials' application. Therefore, the synthesis of satisfactory fibrous material has been the interests among researchers. In this article, we expect to synthesize a kind of fibrous material which can be preferably applicable for aqueous arsenic removal. We select polyacrylonitrile (PAN) fiber as the matrix material. The nitrile group in the structure of PAN polymers is able to participate in many variable chemical reactions.[13] We select ethylenediamine as the reactant because ethylenediamine shows faster reactive velocity in the synthesis
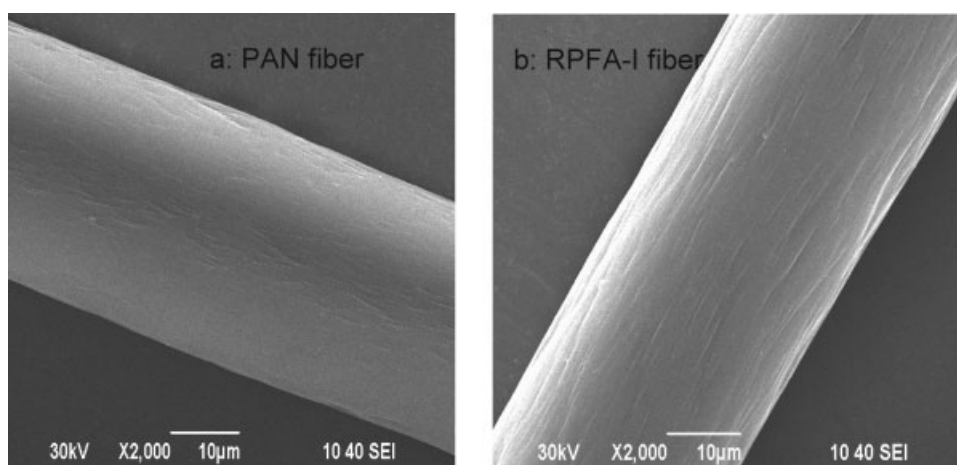
Figure 1 S.E.M of PAN and RPFA-I fibers (a) PAN fiber; (b) RPFA-I fiber.

process. And if the amino groups can be grafted to the surface of the PAN fibers, this amino fiber may have good adsorption properties for arsenic.

During the process of synthesis, it must be considered how to reduce the loss of the mechanical properties of the matrix fiber. So we synthesize RPFA-I fiber by two steps. First, PAN is crosslinked with hydrazine to reduce the loss of the fiber's mechanical properties, and then the product in the first step is reacted with the reactant ethylenediamine to obtain the amino functional groups. Also the amino modification, properties, and application of the RPFA-I fibers have been investigated through scanning electron microscope (SEM), Fourier transform infrared (FTIR), auto-tensile tester, and batch of adsorption experiments.

EXPERIMENTAL SECTION

Preparation of Rpfa-I ion exchange fiber

RPFA-I ion exchange fiber is a kind of functional fibrous material with amino groups which has been synthesized in our lab. After cleaned and dried, PAN fiber was added to the hydrazine (15%) solution with the mass ratio 1 : 40. Heated for 5 h, then cooled and washed to exclude the hydrazine.[13] After that, dried the fiber again and weighed. The weight of the fiber in this process was increased by 8–12%. The product in this course is called C-PAN.

One gram of C-PAN was added to glycol (about 30 mL) and ethylenediamine (about 1.0 mL) solution in the 3-neck boiling flask at the temperature of about 110–140°C. The reaction would last more than 2 h. When ended, the fiber was fetched into the deionized water to be washed to neutrality. Then after drying, the product RPFA-I ion exchange fiber was obtained.

Characterization of Rpfa-I ion exchange fiber

SEM (JSM-6390LV) with 30-kV accelerating voltage was used for fiber measurements. Samples were dried overnight at about 45°C in an air oven. They were then mounted on an aluminum stage with carbon tape, and coated using a gold plasma spray for 50 s.

A Labthink XLW (L) PC auto-tensile tester was used for testing the stretching resistance of fibers. Samples were dried at about 45°C in the air oven and 60 fiber filaments were tested for average calculation.

Nicolet IR 200 spectrum analyzer was used for determining the information of functional groups on the fiber. The samples were dried at about 45°C in the air oven. They were then compressed with KBr
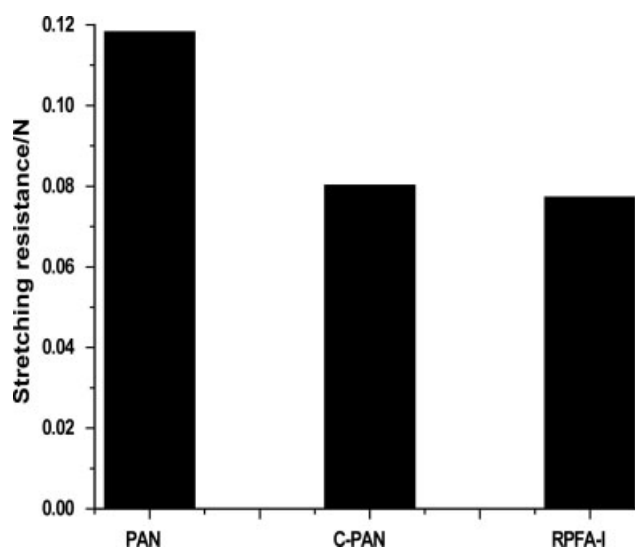

Figure 2 Stretching resistance of PAN, C-PAN, and RPFA-I.

in FW-4A powder sheeter, in which the whole process was operated in HW-3 IR oven.

Adsorption experiments

Preparation of arsenic stock solution

Sodium arsenate ($Na_2HAsO_4.7H_2O$; AR) and sodium arsenite ($NaAsO_2$; AR) were used as arsenic sources. A stock solution of arsenic was prepared at the concentration of 100 mg/L with the deionized water. The pH of the solution was adjusted to 7.0 using 0.1 mol/L HCl or NaOH solutions. The stock solution would be diluted during the course of experiment.

The effect of pH value on arsenic removal

PHS-3E pH meter was used for pH measurements after calibration with the dilute HCl or NaOH. Fibers were weighed exactly 25 mg per share. Fifty milliliter of arsenic solution and 25 mg of RPFA-I were added to a 100-mL conical flask. The initial arsenic concentration was 5 mg/L, and the pH was in the range of 4–12. All samples were set into a to-and-fro shaker at $(25 \pm 0.5)°C$. After 12 h, each share of the solution was passed through the filter paper. Inductively coupled plasma atomic emission spectrometry (ICP-AES, TJA advantage) was used for residual arsenic analysis.

Adsorption isotherm

A series of 100-mL conical flasks were added to 25 mL of arsenic solutions with the concentration of 1– 5 mg/L and a certain amount of RPFA-I fibers. All samples were shaken in a to-and-fro shaker for 12 h at $(25 \pm 0.5)°C$. After that, the solution was passed through the filter paper and residual arsenic was analyzed by ICP-AES. The data of arsenic adsorption
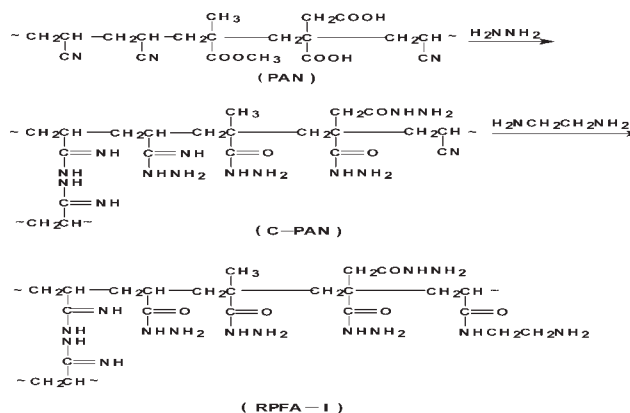
Figure 3 The reaction mechanism about crosslinking and chemical modification.

was analyzed by Freundlich/Langmuir isotherm models.

Adsorption dynamics

Twenty-five milliliters of arsenic solution and 150 mg of RPFA-I fiber were added, respectively, in a series of 100-mL flasks. The initial arsenic concentration was 5 mg/L. The suspension was stirred and the temperature was kept at room temperature. At regular time intervals, the solution with residual arsenic in a certain flask was filtered for arsenic analysis. The dynamic data was described by the pseudosecond-order kinetic mode.

Regeneration

0.1 mol/L NaOH solution was used for arsenic desorption. Two hundred milligrams fiber and 100 mL arsenic solution were added into the 250-mL flask. The mixture was shaken at room temperature for almost 12 h. The used fibers were cleaned by deionized water and dried for desorption with dilute NaOH. After desorption, the fiber was eluted with
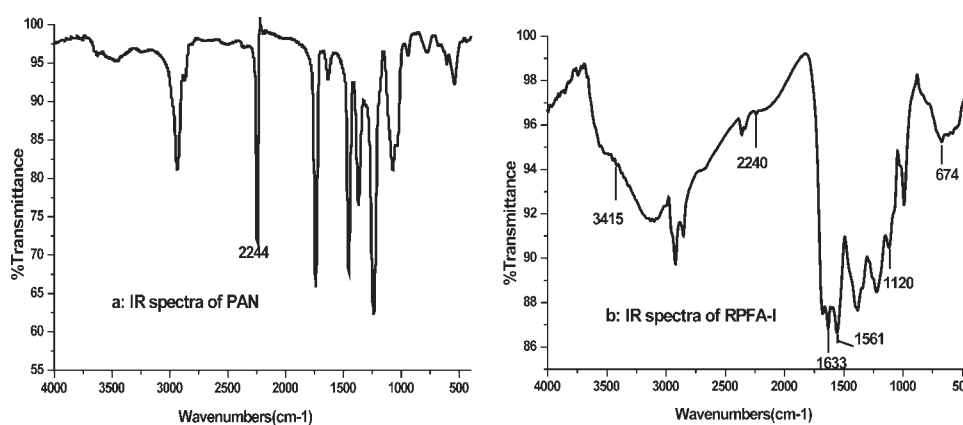
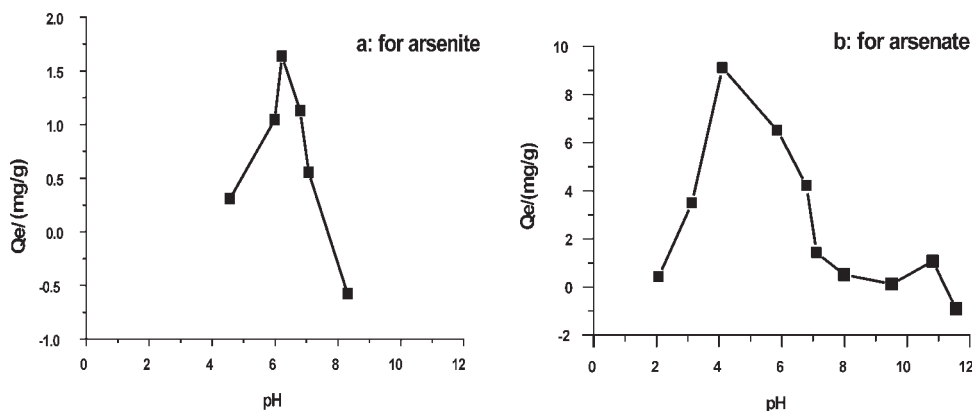**Figure 4** IR spectra of PAN and RPFA-I (a) PAN fiber; (b) RPFA-I fiber.

Figure 5 The effect of pH value on arsenite and arsenate adsorption [(a) for arsenite; (b) for arsenate].

deionized water several times to neutrality. This process lasted long for avoiding incomplete desorption because static test was just done here.

RESULTS AND DISCUSSION

SEM and stretching resistance studies

It is important for materials to keep fine mechanical property during the stage of chemical modification. A remarkable advantage of fiber materials is that it can be applied in many forms such as filament, thread, nonwoven cloth, and other textile items. Therefore, it is important not to change the fiber form of the matrix during chemical modification. In this article, matrix PAN fiber is crosslinked with hydrazine before chemical modification. Figure 1 shows the SEM images of PAN and RPFA-I fibers.

In comparison with PAN, though the surface of RPFA-I is smooth, there're still more channels and deeper marks on the surface. Nevertheless these channels are distributing uniformly. This indicated that there were some defects in fibers after crosslinking and modification. However, these defects, induced by

the reaction between nitrile groups and reactants, will probably lead to the loss of the mechanical properties (mainly the stretching resistance) of the fiber, they make the fibers' specific surface area larger, and that's just the reason why fiber materials are preferable during ion-exchanging process.

Figure 2 shows the average value of the stretching resistance for 60 fiber filaments tested by the auto-tensile tester. The average stretching resistance of PAN was about 0.118 N but after croslinking, the average stretching resistance of C-PAN was 0.080 N, and after chemical modification, the average stretching resistance of RPFA-I was 0.077 N. The ratio of reduction was 35% compared with the average stretching resistance of the PAN fibers.

FTIR studies

According to Refs. 13,15,16, the reaction mechanism about the synthesis process is illustrated in Figure 3.

We did IR analysis for determining the information of functional groups. Figure 4 shows the IR spectra of PAN and RPFA-I. From the IR spectra of PAN [Fig. 4(a)], the nitrile functional group was
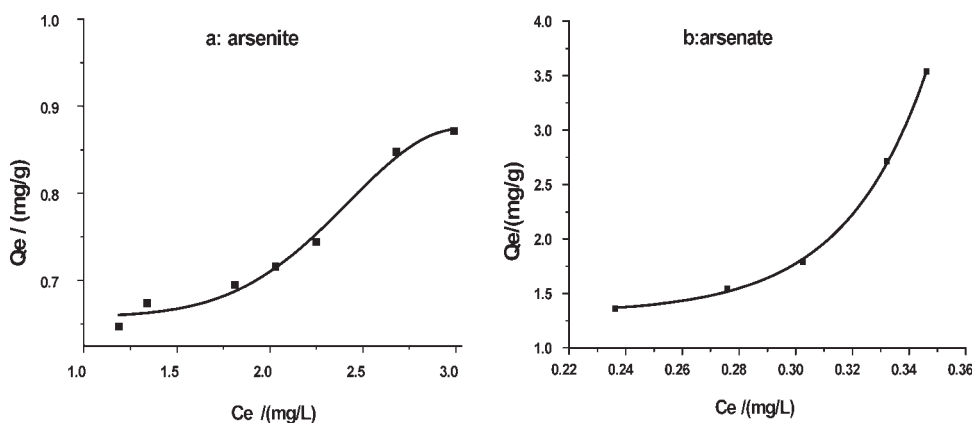

Figure 6 The relationship of equilibrium concentration and adsorption capacity for arsenite and arsenate [(a) arsenite; (b) arsenate].

TABLE I
The Relative Coefficients of Langmuir/Frundlich Isotherm Equation
for Arsenite and Arsenate

	Langmuir			Frundlich		
	$Q/(\text{mg g}^{-1})$	b	R^2	K	n	R^2
Arsenite	1.6266	1.6009	0.9971	1.9797	1.9853	0.9784
Arsenate	9.1895	0.1886	0.9817	0.0261	0.3089	0.9244

very clear (2244 cm^{-1}, strong, sharp), and after crosslinking and modification [Fig. 4(b)], the adsorption peak of nitrile group appeared weak and almost disappeared (2240 cm^{-1}), but the adsorption peaks concerned showed meantime, that is, 3415 cm^{-1} (NH$_2$, N—H symmetric stretching), 1633 cm^{-1} (NH$_2$, N—H in-plane deformation), 1561 cm^{-1} (NH deformation and C—N stretching), 1120 cm^{-1} (C—N stretching), 674 cm^{-1} (NH$_2$, N—H out-of-plane deformation). These show that the amino functional group anticipated has been obtained.

Sorption studies

Effect of pH values

Arsenic is present in water in several forms depending on the pH value and the redox potential. At typical pH values in natural water (pH 5–8), two oxidation states are commonly found: arsenite As(III) mainly exists fully protonated (H$_3$AsO$_3$) and arsenate As(V) remains as an anion, which could be found in various species in the dissolved form such as H$_2$AsO$_4^-$ and HAsO$_4^{2-}$.[17]

The pH value determines the predominant species present in water and is therefore expected to be a very influencing parameter during arsenic removal treatments. Figure 5(a) shows the effect of pH value on RPFA-I for arsenite removal. When pH = 6.2, adsorption capacity reached to a maximum. The rea-

son may be: when pH < 7.0, H$_3$AsO$_3$ is predominant, but when pH increases, the content of it decreases gradually[1]; So RPFA-I may have more preferential adsorption for H$_3$AsO$_3$ than other arsenite species. Furthermore, OH$^-$ increases correspondingly with pH increasing and will compete with arsenite species to occupy the efficient exchange sites on the surface of RPFA-I, which may be another reason why the adsorption capacity for arsenite decreased when pH increased. Figure 5(b) shows the effect of pH values on RPFA-I for arsenate removal. When pH = 4.1, the adsorption capacity reached to a maximum. When the pH was in the range of 3.9–6.1, the adsorption capacity was above 5 mg/g, but when pH > 6.2, it decreased. The reason may be: when pH is in the range of 3.0–6.0, H$_2$AsO$_4^-$ is predominant but decreases with the increasing pH[1]; this shows RPFA-I may have more excellent preferential adsorption for H$_2$AsO$_4^-$ than it for other arsenate species.

Adsorption isotherm

Figure 6 shows the relationship between equilibrium concentration and adsorption capacity. From Figure 6(a), the adsorption capacity increased gradually with the increasing concentration. The adsorption capacity for arsenate also increased with the increasing arsenate concentration [Fig. 6(b)].
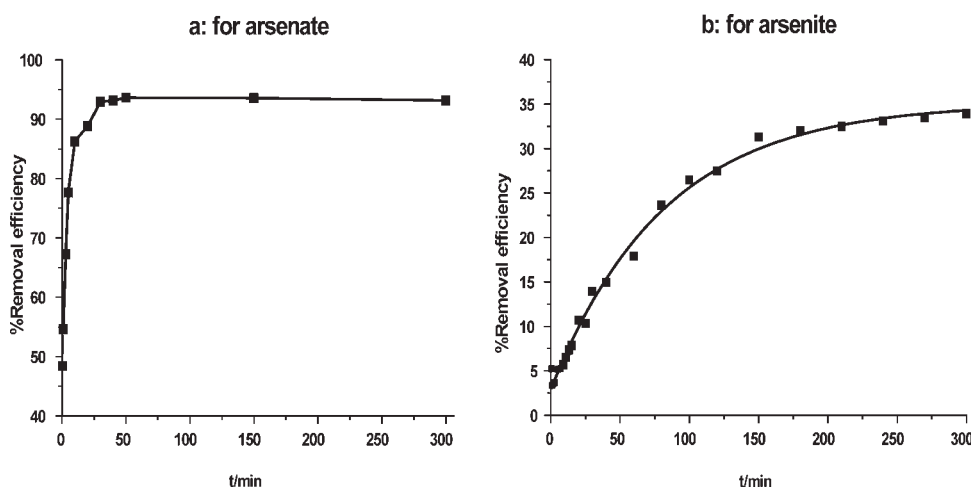

Figure 7 Adsorption kinetic curve of RPFA-1 ion exchange fiber for arsenate and arsenite [(a) for arsenate; (b) for arsenite].
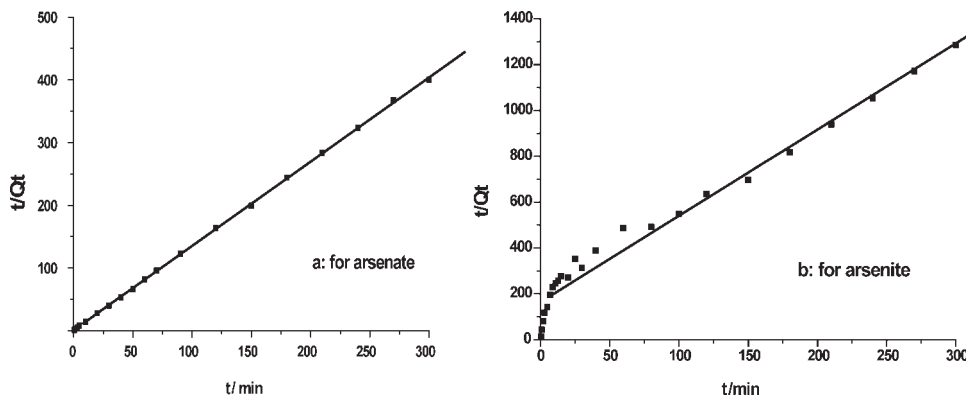
Figure 8 Lagergren second-order rate equation of RPFA-I for arsenate and arsenite [(a) for arsenate; (b) for arsenite].

Two groups of equilibrium data can be simulated by Freundlich equation and Langmiur equation.

The Langmuir isotherm is expressed as follows:

$$Q_{eq} = bQ_{max}C_{eq}/(1 + bC_{eq}) \qquad (1)$$

where Q_{max} (mg/g) is the maximum adsorption capacity, C_{eq} (mg/L) is the equilibrium solute concentration, Q_{eq} (mg/g) is the adsorption capacity at equilibrium, and b is the equilibrium constant related to the energy of sorption (L/mg). The equation can be changed as follows:

$$C_{eq}/Q_{eq} = 1/(bQ_{max}) + C_{eq}/Q_{max} \qquad (2)$$

so b and Q_{max} values can be determined experimentally by plotting C_{eq}/Q_{eq} versus C_{eq}.

The Freundlich isotherm is expressed as follows:

$$Q_{eq} = KC_{eq}^{1/n} \qquad (3)$$

where K is the empirical constant ((mg/mL)/(mmol/L) 1/n) and n is the empirical constant (dimensionless).The equation can be changed as follows:

$$\log Q_{eq} = \log k + 1/n \times \log C_{eq} \qquad (4)$$

the values of k and n can be determined experimentally by plotting $\log Q_{eq}$ versus $\log C_{eq}$.

Table I shows the relative coefficients.

Adsorption kinetics

The fascinating factor of fibrous adsorbents is the excellent adsorption kinetics. Figure 7 shows the kinetic curve of RPFA-I for arsenate and arsenite. The kinetic data was described by Lagergren pseudo-second order rate equation, which the equation is expressed as follows:

$$dQ_t/dt = k_2(Q_{eq} - Q_t)^2 \qquad (5)$$

where Q_{eq} is the sorption capacity at equilibrium and Q_t is the solid-phase loading of arsenic at time t. k_2 (mL mg^{-1} h^{-1}) represents the pseudo-second order rate constant for the kinetic model. By integrating the equation with the boundary conditions of $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$, the following linear equation can be obtained:
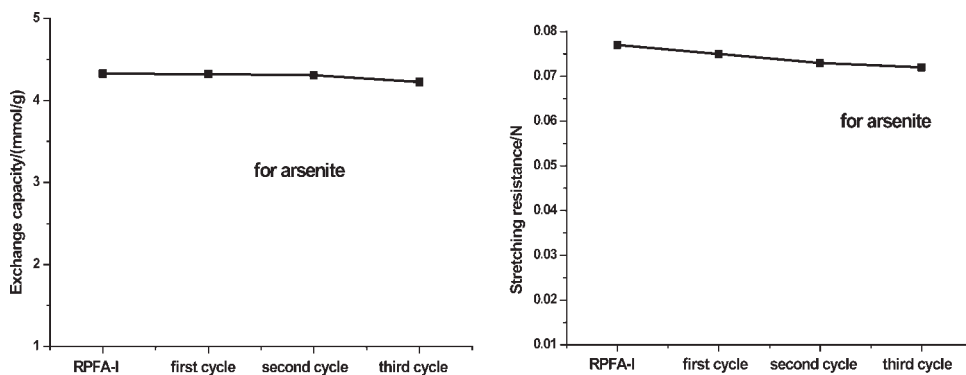

Figure 9 The exchange capacity and stretching resistance of RPFA-I after three cycles of arsenite adsorption and regeneration.
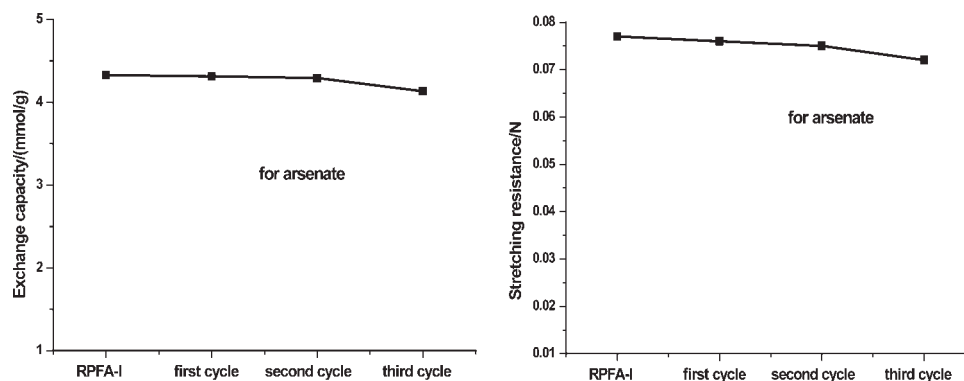
Figure 10 The exchange capacity and stretching resistance of RPFA-I after three cycles of arsenate adsorption and regeneration.

$$t/Q_t = 1/V_0 + t/Q_{eq} \qquad (6)$$

$$V_0 = k_2 Q_{eq}^2 \qquad (7)$$

where V_0 (mg mL^{-1} h^{-1}) is the initial sorption rate. Therefore, the V_0 and Q_{eq} values of kinetic tests can be determined experimentally by plotting t/Q_t versus t.

Figure 7(a) shows the relationship between adsorption time and removal efficiency for arsenate adsorbed on RPFA-I. In a about 30 min, the adsorption equilibrium was achieved and the removal efficiency was above 93%.The kinetic data can be well described by Lagergren pseudo-second order rate equation, the relative coefficient was 0.9998, and the adsorption rate constant was 2.1219 min^{-1} [Fig. 8(a)]. But RPFA-I didn't show better adsorption results for arsenite [Fig. 7(b)]. The adsorption equilibrium hasn't been achieved in 300 min and the removal efficiency was less than 35%. Adsorption time was then prolonged to 12 h and about 70% of arsenite was removed by RPFA-I. The kinetic data was described using Lagergren pseudo-second order rate equation, the relative coefficient was 0.9707, but the adsorption rate constant was just 0.0494 min^{-1} [Fig. 8(b)].

Regeneration studies

A regeneration study was conducted where RPFA-I fiber samples were taken through a series of exhaustion and regeneration cycles with 0.1M NaOH solution. From Figures 9 and 10, the exchange capacity of the fibers was almost constant and the stretching resistance changed a little after three cycles. This indicates that regeneration of RPFA-I fibers is possible, and the procedure of regeneration is simple and practical.

CONCLUSIONS

The ion-exchange fiber RPFA-I discussed here has resulted in a number of significant advantages over other materials, such as the fast rate of adsorption, uncomplicated nature of process techniques (including the preparation of the material and the adsorption process), and simple procedure for regeneration.

On the basis of the results of tensile and SEM test, RPFA-I fibers keep fine mechanical properties of the matrix material, and the active functional group (amino groups) is confirmed by the IR analysis. The adsorption experimental results show that RPFA-I has higher adsorption capacity and fine adsorption kinetics during the process of arsenic removal. RPFA-I has a good sensitivity to arsenic with lower concentration (5 mg/g), so that RPFA-I can be used for deep purification in water with arsenic. And the spent RPFA-I can be regenerated by dilute NaOH conveniently.

References

1. Smedley, P. L.; Kinniburgh, D. G. Appl Geochem 2002, 17, 517.
2. Ng, K. S.; Zaini, U.; Pierre, L. C. Rev Environ Sci Biotech 2004, 3, 43.
3. Ruthann, R.; Tracey, M. S.; Barbara, D. B. Regulat Toxicol Pharm 1996, 23, 87.
4. Knowles, F. C.; Benson, A. A. Trends Biochem Sci 1983, 8, 178.
5. Hughes, M. F. Toxicol Lett 2002, 133, 1.
6. Sun, G. F. Environ Sci 2001, 8, 425.
7. Gu, Z. M.; Fang, J.; Deng, B. L. Environ Sci Technol 2005, 39, 3833.
8. Younghun, K.; Changmook, K.; Inhee, C.; Selvaraj, R.; Jongheop, Y. Environ Sci Technol 2004, 38, 924.
9. Kundu, S.; Gupta, A. K. Eng J 2006, 6, 4864.
10. Monica, C. T.; Virgianias, T. C. Environ Sci Technol 2005, 39, 895.
11. Chanda, M. O.; Driscoll, K. F.; Rempel, G. L. React Polym 1988, 7, 251.
12. Guo, X. J.; Chen, F. H. Environ Sci Technol 2005, 39, 6808.
13. Soldatov, V. S.; Pawlowski, L.; Shunkevich, A. A.; Wasag, H. New Materials and Technologies for Environmental Engineering. Part I. Syntheses and Structure of ION Exchange Fibers, Lublin, 2004.
14. Anirudhan, T. S.; Unnithan M. R. Chemosphere 2006, 66, 60.
15. Zheng, B. W., Fischer, K. Bieniek, D.; Kettrup, A. React Polym 1994, 24, 49.
16. Zhou, L.; Zhou, S. Ion Exchange Adsorp (In Chinese) 1993, 9, 486.
17. Kartinen, E. O.; Martin, C. J. Desalination 1995, 103, 79.