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Research on Preparation of Sheath-Core Bicomponent Composite Ion Exchange Fibers and Absorption Properties to Metal Ion

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Abstract: Based on the sheath-core bicomponent composite fibers with modified polystyrene (PS) and the modified polypropylene (PP), composite fibers obtained were further cross-linked and sulphonated with chlorosulphonic acid to produce strong acidic cation ion exchange fibers. The structures of the fibers obtained were characterized using Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) etc. The optimal technology of the fibers obtained is discussed. The static absorption capacity of the sheath-core bicomponent composite cation exchange fibers for Zn^{2+}, Cu^{2+} was determined. The absorption kinetics and major factors affecting the absorption capacities of Zn^{2+}, Cu^{2+} were studied, and its chemical stability and regenerating properties were probed. The results suggest that cation exchange fibers with better mechanical properties and higher exchange capability were obtained. Moreover, this type of ion exchange fiber has good absorption properties and working stability to various metal ions. Hence, they have higher practicability.

Keywords: sheath-core bicomponent composite ion exchange fibers, cross-linkage, sulphonation, structure, metal ions, absorption property.

Introduction

Ion-exchange fiber is a fiber-form ion-exchange material. It has bigger specific surface area, faster rate of exchange and elution, higher regeneration performance, lower consumption, smaller fluid resistance than that of ion-exchange resin.[1,2] It can be applied in many kinds of forms such as fiber, cloth, nowoven etc, and can be applied to various of exchange processes. The ion exchange fibers are suitable for adsorption separation of toxic metal ion and selective concentration of the trace element because of its faster rate of exchange and elution, so they are applied as higher efficient adsorption separation materials.[3-8] The sheath-core bicomponent composite ion exchange fiber made from modified PS[9] as sheath and the modified PP[10-12] as core is successfully obtained, it has some advantages, such as lower manufacture cost, simple process, good usage of the existing facilities etc, so it is a new type of ion-exchange fiber method with promising prospects. But the compatibilization of sheath-core fiber is so bad that its functionseses is different from that of original fiber, so that the mechanics functionseses of the fiber with lower exchange capacity can not be suitable for the needs in the post-treatment step. In this paper, based on the sheath-core bicomponent composite ion exchange fibers with the modified PS and the modified PP, we gained the cation exchange fibers with mechanical property and higher exchange capability. The static exchange capacity of the sheath-core cation ion exchange fibers on metal ion are measured, and the absorption kinetics and the main factors affecting absorption capacities are studied as an example of Zn^{2+} and Cu^{2+}, its chemical stability and regenerating property are probed, and it has high practicability.

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Experimental

Materials and Spinning Machine. Self-made original sheath-core bicomponent composite fiber made from the modified PS as sheath and the modified PP as core.[13,14] Polypropylene (PP) was provided from Shanghai Petro-Chemical Co.Ltd, China. Its characteristics commonly used for fibers spinning are as follows: Mn: 1.7×10^5, MI: 39.0 g/10 min (230 °C), density: 0.92 g/cm^3, and polydispersity: 3.8. Polystyrene (PS) was provided from Shanghai Petro-Chemical Co.Ltd, China. Its characteristics commonly used for fibers spinning are as follows: Mn: 1.1×10^5, MI: 31.0 g/10 min

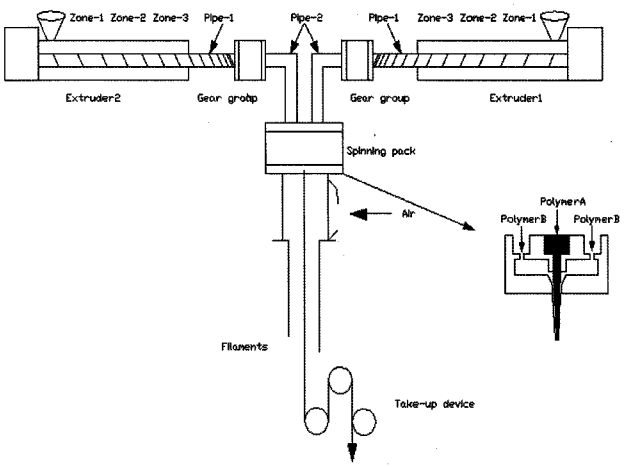

Figure 1. Schematic diagram for the bicomponent fibers spinning system.

(260 °C), density: 1.08 g/cm^3. The spinning machine was a general conjugate spinning machine, which was composed of two extruders ($L/D = 25$, $D = 20$ mm) and gear pumps. The Figure 1 illustrates the spinning system used fore generating sheath-core bicomponent fibers.

The Preparation of Sheath-Core Bicomponent Composite Ion Exchange Fiber.

Cross-linkage Reaction: The sheath-core bicomponent composite fibers obtained were cut into staple fibers with 0.5 centermeter, and the staple fibers were cleaned by detergent and methanol respectively so as to remove oils and impurities on the surfaces of fibers, and were dried fully in oven. Weigh some amounts of original fibers, put them into the bottle to sulphonate at 50-70 °C for 2-6 h while joining concentrated sulphuric acid, glacial acetic acid and paraformaldehyde respectively, keep stirring in the process to gain the brown yellow cross-linkage products.

Sulphonation Reaction: Joining concentrated sulphuric acid and 1,2-dichloroethane respectively, the cross-linkage products were sulphonated for 1-4 h at constant temperatures of 75-90 °C, keep stirring in the process to gain the sulphonation products, which were diluted with different concentration sulphuric acid, then washed again and again using de-ionized water until the flushing water showed neutral, dried in the air naturally to gain the strong acidic cation exchange fibers.

Measurement of the Static Exchange Capacity. After washing the sample of sheath-core bicomponent composite ion exchange fibers obtained for many times using de-ionized water, it was dried to keep no water in the vacuum. Weigh 0.2 grams of dried fiber accurately, put it into 200 milliliters of tapers bottle, accurately join the standard aqua NaOH (0.1 mol/L) of 30 mL and the istilled water of 30 mL, respectively, oscillate and remove the spirit attached on the fiber bubble, seal completely to place certain time. Then titrate using the standard hydrochloric acid aqua (0.1 mol/L), according to the whole exchange capacity measurement method of cation exchange resin on wet subbase in documents, calculate the saturated ion exchange capacity using the following equation:

$$Q_w = (V_0 - V_1) \times C/m$$

In the type: Q_w: adsorption capacity of the fiber (mmol/g)
C: the concentration of standard hydrochloric acid aqua (mol/L)
V_0: the hydrochloric acid aqua physical volume that consumed in titrating the blank (mL)
V_1: the hydrochloric acid aqua physical volume that consumed in titrating the sample (mL)
m: the quantity of the fiber(g)

Measurement of the Static Exchange Capacity on Metal Ion. After the samples of sheath-core bicomponent composite ion exchange fibers obtained are dried to keep equal mass in the vacuum, weigh some amounts of dried fibers accurately, put them into 250 milliliters of tapers bottle, drip down the metal ion solution (0.1 mol/L) of 40 mL accurately. The concentration of metal ion in the solution is measured by complexometric titration using ethylenediamine tetraacetic acid (EDTA), calculate the ion exchange capacity on different metal ion using the following equation:

$$Q = (C_0 - C) \times V/W$$

In the type, Q: adsorption capacity (mmol/g)
C_0: the concentration of metal ions before adsorption (mol/L)
C: the concentration of metal ions after adsorption (mol/L)
W: the quantity of the fibers (g)
V: the solution volume (mL)

Measurement of Absorption Kinetics for Zn^{2+}, Cu^{2+}. Put several parts of equal volume (20 mL) metal ion solution into the taper bottles respectively, adjust them to the expectation value using the buffer solution of appropriate pH value measured (keep the total ion density of solution for 0.005 mol/L and total volume for the 40 mL), once in a while, take out a taper bottle to measure the concentration of remaining metal ions from solution in it using EDTA titration.

Elution and Regeneration Performance of Fibers. Put the fibers that have adsorbed metal ion into elution solution, after shaking them for enough time, take them off to wash until the washing water shows neutral, then dry naturally to get the regeneration fibers. Put the regeneration fibers into copper sulfate solution with adsorption and elution circulations for 5 times. Then examine heat-proof performance, the chemistry stability, the adsorption capacity and micromorphology variety of fibers, respectively.

Micromorphology Observation. The fibers obtained in different conditions were made into the samples, then were goldsputtered, morphology and structure on the surface of the fibers was observed using scanning electron microscope

(SEM, Quanta 200).

Thermal Analysis. For thermodynamic experiment, dynamic scanning calorimeter (DSC, Perkin-Elmer DSC-7) equipped with a cooler was used under the nitrogen atmosphere. All the samples were heated from 0 to 250 °C at 10 °C/min.

Results and Discussion

The Structure of Sheath-Core Bicomponent Composite Ion Exchange Fiber. Fourier transform infrared spectrophotometry diagrams of all the fibers are depicted in Figure 2. Figure 2 shows that (a) shows FT-IR curve of sheath-core bicomponent composite fiber, (b) shows FT-IR curve of sheath-core bicomponent composite fiber with cross-linkage at 60 °C for 4 h, (c) shows FT-IR curve of sheath-core bicomponent composite fiber with sulphonation at 85 °C for 2 h. It is clear from the figure that broad and strong peak in the range from 1118 to 1221 cm^{-1} is the absorption peak of sulfonic groups, it is explained that the fibers are sulfonated by sulfuric acids in the reaction. The absorption peaks situated at 695 and 755 cm^{-1} in infrared spectroscopy disappear nearly and change into the single peak at 834 cm^{-1}, the fingerprint peak which characterizes substituted position of benzene wreath changes into single peak from double peaks,[15] this explains that the para-substituted structure of benzene wreath replaces of the monosubstituted structure of it in sulphonation reaction, this is to say, para-benzene wreath connects with sulfonic groups only because of big steric hindrance of ortho benzene wreath. Absorption peak of styrene at 1026 cm^{-1} splits into double peaks at 1028 and 1001 cm^{-1} with the increment of sulphonation degree, because in-plane rupture vibration of C-H in the benzene wreath is subjected to the influence of symmetrical stretching vibration of S = O. The polar groups connected with polystyrene in the sulphonation reaction make the fibers hydrophilic, and water absorbency of products is gradually higher with the increment of sulphonation degree. Seen from the diagram, it appears a stronger and broader absorption peak at

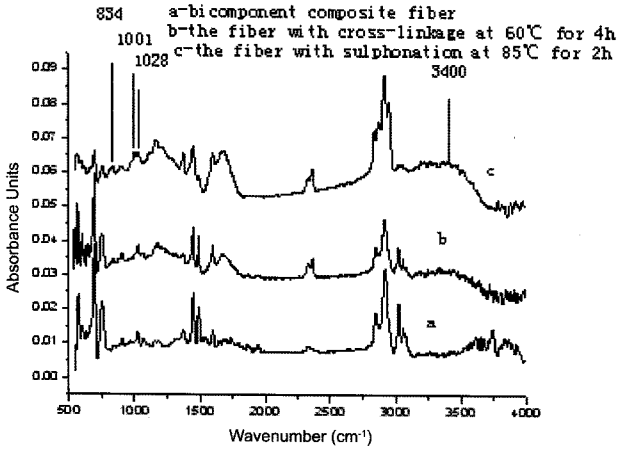

Figure 2. Infrared spectra of fibers.

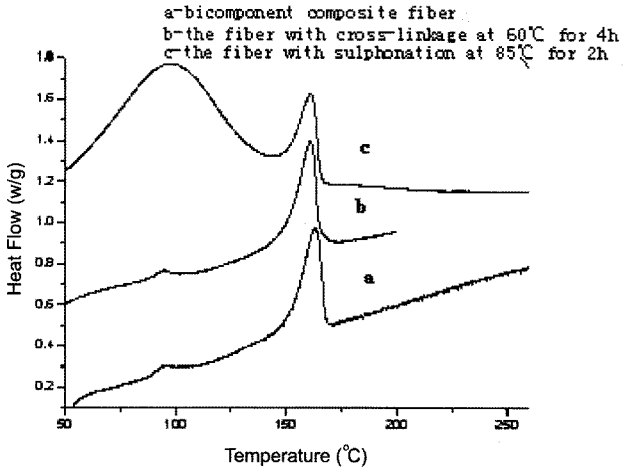

Figure 3. DSC diagrams of fibers.

3400 cm^{-1}, this is because the interaction between hydrogen bond and oxygen atom of sulfonic groups in water molecules makes the stretching vibration absorption peak of -OH displace in the direction of low frequency.[16]

Thermal Property. Differential scanning calorimetry thermograms of all the fibers are depicted in Figure 3. Figure 3 shows that (a) shows DSC curve of sheath-core bicomponent composite fiber, (b) shows DSC curve of sheath-core bicomponent composite fiber with cross-linkage at 60 °C for 4 h, (c) shows DSC curve of sheath-core bicomponent composite fiber with sulphonation at 85 °C for 2 h. The curve (b) compared with the curve (a), T_g of polystyrene keeps no variety, this explains that the fiber is not sulphonated but cross-linked in the cross-linkage reaction. The curve (c) compared with the curve (b), a very strong peak appears from 47.31 to 142.37 °C, this is because that the fibers were connected with very strong polar sulfonic groups to strengthen hygroscopicity of fiber. Moreover, the melting point of polypropylene keeps no variety, this explains that the chemistry stability of modified polypropylene in the core of fiber is very good, and it plays the role of skeleton support.

The Affected Factors of Preparing Sheath-Core Bicomponent Composite Ion Exchange Fiber.

Effect of Cross-linkage Time on Capacity of Ion Exchange Fibers: The exchange fibers with different cross-linkage were obtained on the following conditions: 6 g of the fiber, 5 g of $(CH_2O)n$, H_2SO_4(98%) 150 mL, CH_3COOH 25 mL, $C_2H_4Cl_2$ 7.5 mL, and cross-linked at 60 °C, sulphonated at 85 °C for 2 h. Figure 4 shows the trend that capacity of ion exchange fiber increases first and decreases later with the prolongation of cross-linkage reaction time, the exchange capacity attains the biggest value with better mechanical property while sulphonation time is 4 h or so. Lower than 4 h, the fibers were damaged seriously, the sheath appeared the crack. But the cross-linkage reaction time was too longer, the ion exchange fibers with better mechanical property but lower exchange capability were obtained.

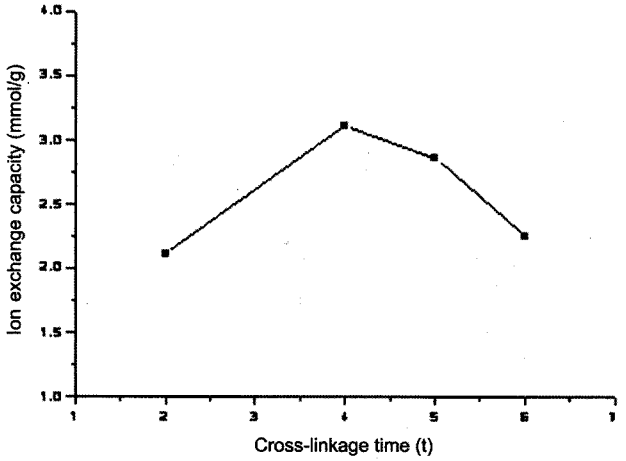

Figure 4. Effect of cross-linkage time on capacity of ion exchange fiber.

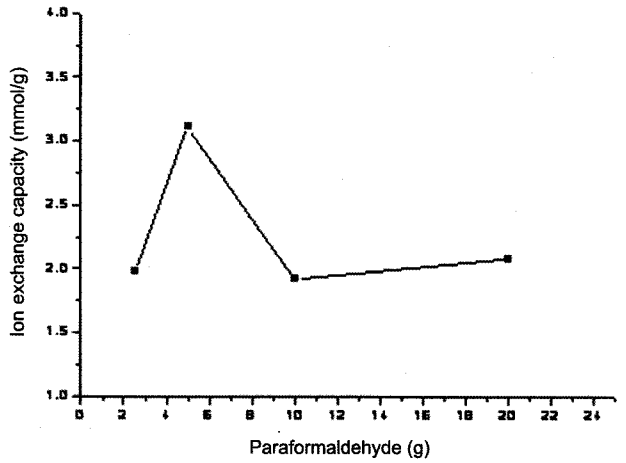

Figure 5. Effect of dosage of paraformaldehyde on ion exchange fiber capacity.

Effect of Concentration of Paraformaldehyde on Capacity of Ion Exchange Fibers in the Reaction Bodies: The exchange fibers with different concentration of paraformaldehyde were obtained on the following conditions: 6 g of the fiber, H_2SO_4(98%) 150 mL, CH_3COOH 25 mL, $C_2H_4Cl_2$ 7.5 mL, and cross-linked at 60 °C for 4 h, sulphonated at 85 °C for 2 h. Figure 5 shows the trend that capacity of ion exchange fiber increases first and decreases later with the increment of the paraformaldehyde, the exchange capacity attains the biggest value while the weight of paraformaldehyde is 5 g. The dosage of paraformaldehyde impacts ion exchange capacity of the fibers greatly: little dosage of paraformaldehyde can not make the fiber gain the efficient cross-linkage degree, this will make the sulfonated PS dissolve in the aqua, so that both sulfonation efficiency and ion exchange capacity are decreased. The excessive dosage leads to too higher degree of cross-linkage, it not only takes up the live position of the benzene wreath, but also makes

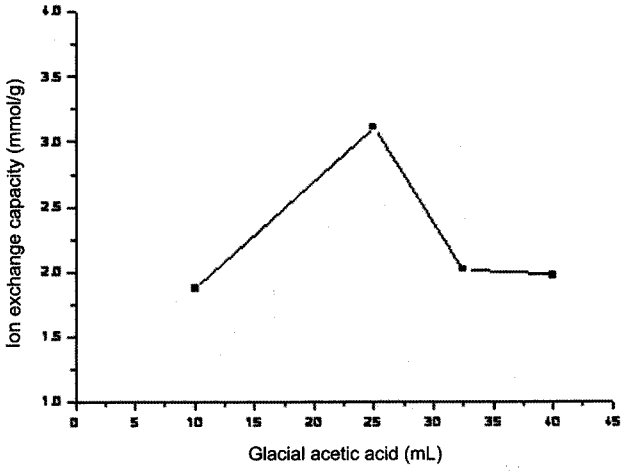

Figure 6. Effect of dosage of glacial acetic acid on capacity of ion exchange fiber in reaction bodies.

the layer of fiber on surface too tighter, so that reduces the live positions in the sulfonation reaction, ion exchange capacity also decreases.

Effect of Concentration of Glacial Acetic Acid on Capacity of Ion Exchange Fibers in the Reaction Bodies: The exchange fibers with different concentration of glacial acetic acid were obtained on the following conditions: 6 g of the fiber, 5 g of $(CH_2O)n$, H_2SO_4(98%) 150 mL, $C_2H_4Cl_2$ 7.5 mL, and cross-linked at 60 °C for 4 h, sulphonated at 85 °C for 2 h. Figure 6 shows that the trend that capacity of ion exchange fiber increases first and decreases later with the increment of glacial acetic acid, the exchange capacity attains the biggest value with better mechanistic property while the dosage of glacial acetic acid is 25 mL or so. Lower or higher than 25 mL, capacity of ion exchange fiber decreases correspondly, especially lower than 25 mL, morphology of fibers is so worse that the crack appears on the sheath of it. Joined a little amount of acetic acid in reaction bodies, which invades amorphous phase of PS to extend molecule crevice mutually as small organic molecules while decreasing the concentration of sulfuric acid, so this can promote utilization ratio of paraformaldehyde. At the same time, efficient degree of cross-linkage can make the benzene wreath of the sheath connect together to improve strength of fiber.

Effect of Sulphonation Time on Capacity of Ion Exchange Fibers: The exchange fibers with different sulphonation time were obtained on the following conditions: 6 g of the fiber, 5 g of $(CH_2O)n$, H_2SO_4(98%) 150 mL, CH_3COOH 25 mL, $C_2H_4Cl_2$ 7.5 mL, and cross-linked at 60 °C for 4 h, sulphonated at 85 °C. Figure 7 shows the trend that capacity of ion exchange fiber increases first and decreases later with the prolongation of sulphonation time, the exchange capacity attains the biggest value with better mechanistic property while the sulphonation time is 2 h or so. Lower than 2 h, the ion exchange fibers with better mechanical property but

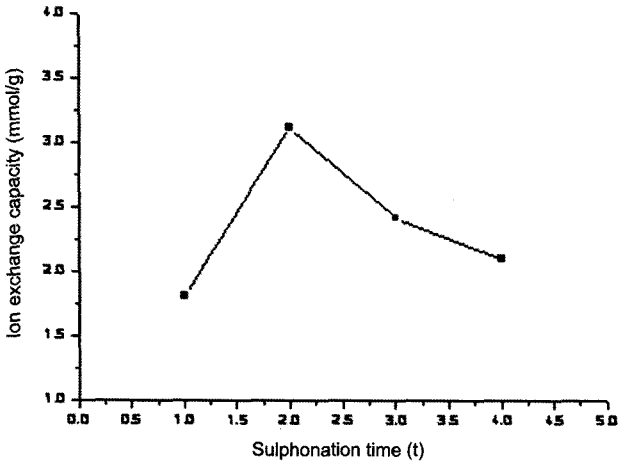

Figure 7. Effect of sulphonation time on capacity of ion exchange fiber.

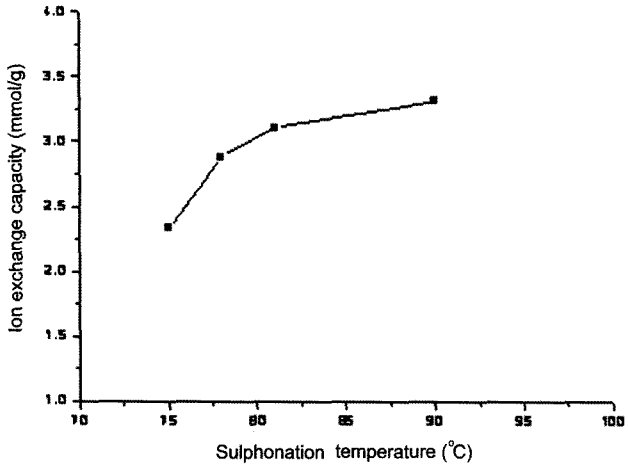

Figure 8. Effect of the sulphonation temperature on ion exchange fiber capacity.

lower exchange capacity were obtained, but the sulphonation time is too longer, it appears slag and even crack, its compatibilization is bad between the sheath and the core of fiber, so strength of fiber is decreasing.

Effect of Sulphonation Temperature on Ion Exchange Capacity of the Fibers: The exchange fibers with different sulphonation temperature were obtained on the following conditions: 6 g of the fiber, 5 g of $(CH_2O)n$, H_2SO_4(98%) 150 mL, CH_3COOH 25 mL, $C_2H_4Cl_2$ 7.5 mL, and cross-linked at 60 °C for 4 h, sulphonated for 2 h. Figure 8 shows that the reaction temperature impacts on ion exchange capacity of the fibers greatly, this is mainly because the reaction will strengthen and expend inside the fiber in accordance with temperature increasing, various of side reaction will also increase when the reaction is strengthening in the sulfonated bodies, thus it is so harm greatly to fibers that the strength of fibers is decreasing but the surface of fibers sheds off easily. Therefore, we gain the ion exchange fibers with better mechanical property and higher exchange capability when the temperature is at 81 °C.

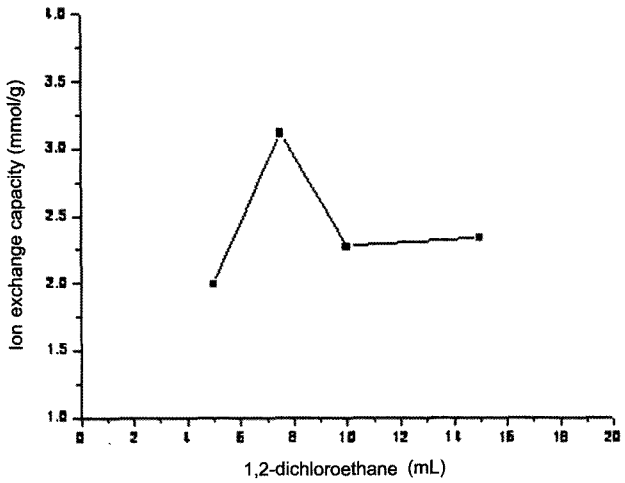

Figure 9. Effect of dosage of 1,2-dichloroethane on capacity of ion exchange fiber in reaction bodies.

Effect of Concentration of 1,2-Dichloroethane on Capacity of Ion Exchange Fiber in the Reaction Bodies: The exchange fibers with different concentration of 1,2-dichloroethane were obtained on the following conditions: 6 g of the fiber, 5 g of $(CH_2O)n$, H_2SO_4(98%) 150 mL, CH_3COOH 25 mL, and cross-linked at 60 °C for 4 h, sulphonated at 85 °C for 2 h.

Figure 9 shows the trend that capacity of ion exchange fibers increases first and decreases later with the increment of 1,2-dichloroethane, the exchange capacity attains the biggest value while the dosage of 1,2-dichloroethane is 7.5 mL or so. The dosage is lower or higher than 7.5 mL, capacity of ion exchange fiber is decreased. Especially higher than 7.5 mL, the sheath of the fibers is damaged seriously because it is subjected to the influence of swelling agent, it appears slag and even crack, its compatibilization is bad between the sheath and the core of fiber, strength of fiber is decreasing. But lower than 7.5 mL, the ion exchange fiber with better mechanical property but lower exchange capability was obtained. Therefore, we gain the ion exchange fiber with better mechanical property and higher exchange capability when the dosage of 1,2-dichloroethane is 7.5 mL.

The Absorption Properties of Sheath-Core Bicomponent Composite Ion Exchange Fiber to Metal Ion.

Absorption Kinetics for Zn^{2+}, Cu^{2+}: Keep the total metal ion concentration from solution for 0.005 mol/L, total volume for the 40 mL and keep the adsorption temperature for 15 °C, while adjust the solution to the best adsorption pH value for Zn^{2+}, Cu^{2+} using the pH buffer solution measured. The adsorption capacity are measured respectively at different adsorption time.

The variations of absorption kinetics for Zn^{2+}, Cu^{2+} are shown in Figure 10. We can see from Figure 10 that the sheath-core bicomponent composite ion exchange fibers have faster

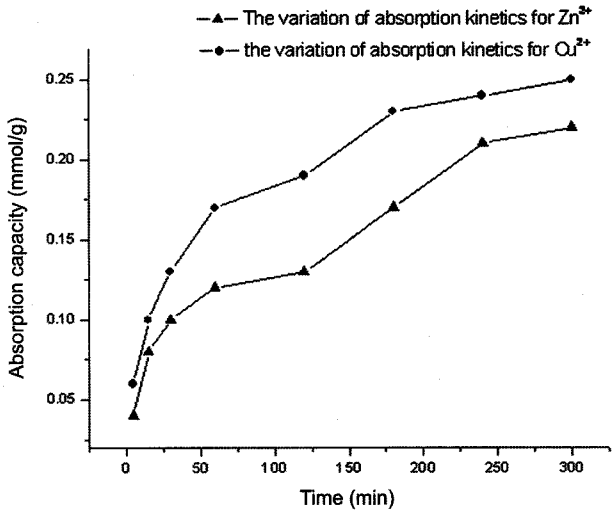

Figure 10. The variation of absorption kinetics for Zn^{2+}, Cu^{2+}.

absorption rate for Zn^{2+}, the absorption capacity for Zn^{2+} can reach to half of equilibrium capacity nearly in 30 min and it can reach to adsorption equilibrium capacity nearly in 4 h. Compared with the absorption rate for Zn^{2+}, the sheath-core bicomponent composite ion exchange fibers have faster absorption rate for Cu^{2+}, the absorption capacity for Cu^{2+} exceed half of equilibrium capacity in 30 min. Moreover, We can see from the diagrams that the absorption capacity of fibers for Zn^{2+}, Cu^{2+} increases quickly in the first one hour and increases slowly after one hour, then increases quickly again in the last two hours. This is explained that the adsorption from sulfonic groups is mainly happened on the sheath surface of fibers, the absorption capacity of fibers increases slowly until the adsorption from sulfonic groups get to saturated. The sheath of fibers begin to swell through soaking for a period of time, the adsorption from sulfonic groups on the deeper layer of the sheath goes on taking place so as to increase the absorption capacity quickly again.

The curve is fitted from data in Figure 10 based on G. E. Boyd equation of liquid film diffusion, which is usually described in the following form:

$$-\ln(1-F) = kt$$

Where $F = Q_t/Q_m$, Q_t represents adsorption capacity at time t (mmol/g); Q_m represents adsorption capacity at equilibrium time (mmol/g); t represents adsorption time (min); k represents liquid film diffusion coefficient. The plots at the given time from the experiment are shown in Figure 11 and Figure 12 respectively.

It is clear from Figure 11 and Figure 12 that the better straight lines are shown between -ln(1-F) and t, explaining that liquid film diffusion is main controlling step,[17] the absorption rates of the sheath-core bicomponent composite ion exchange fibers for Zn^{2+}, Cu^{2+} can be described by liquid film diffusion equation, liquid film diffusion coefficients are

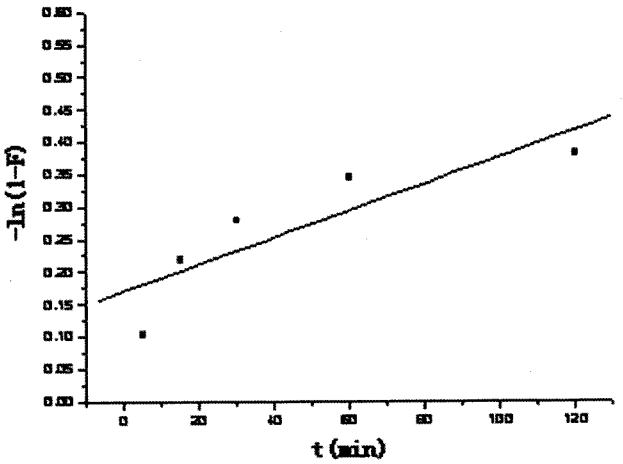

Figure 11. Measurement of adsorption rate coefficient for Zn^{2+}.

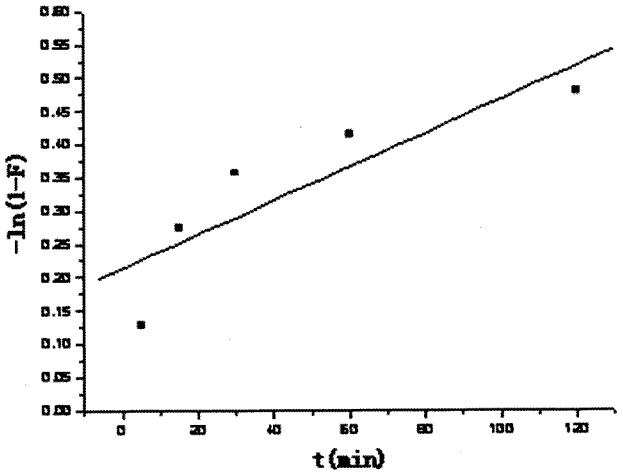

Figure 12. Measurement of adsorption rate coefficient for Cu^{2+}.

Table I. Adsorption Rate Coefficient

Metal Ions	Zn^{2+}	Cu^{2+}
k (min^{-1})	0.00206	0.00254

regarded as adsorption rate coefficients. The adsorption rate coefficient k of the fibers for metal ions are obtained by the linear regression to Figure 11 and Figure 12 respectively, the results are listed in Table I, the parameters in Table I display that the adsorption rate coefficient of Cu^{2+} is bigger than that of Zn^{2+}.

The Affected Factors of Adsorption.

Effect of PH Values on Adsorption: Keep the total metal ions density from solution for 0.005 mol/L, total volume for the 40 mL and keep the adsorption temperature for 15 °C, while keep the same adsorption time. The adsorption capacities are measured respectively at different adsorption pH values.

The variations of absorption capacity for Zn^{2+}, Cu^{2+} with different adsorption pH values are shown in Figure 13. We can see from Figure 13 that the absorption capacity of

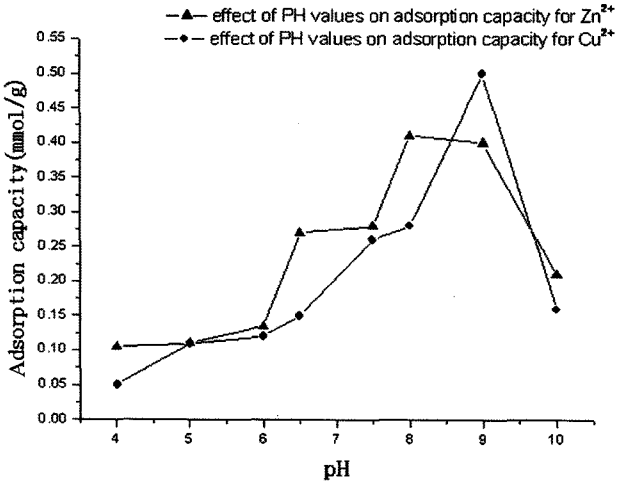

Figure 13. Effect of pH values on adsorption capacity for Zn^{2+}, Cu^{2+}.

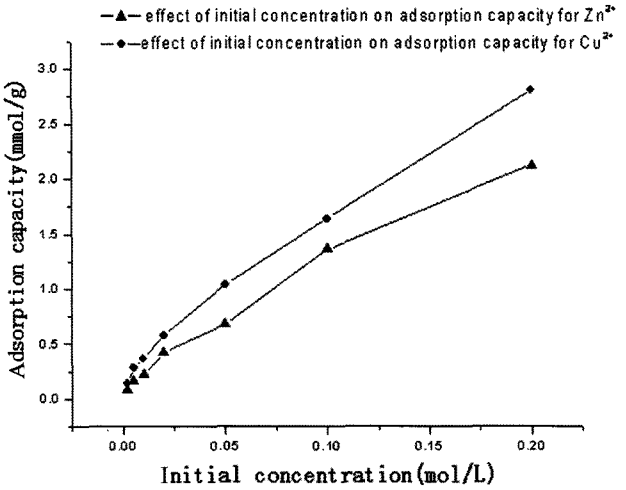

Figure 14. Effect of initial concentration on adsorption capacity for Zn^{2+}, Cu^{2+}.

sheath-core bicomponent composite ion exchange fibers for Zn^{2+} is lower at the small pH values, which reaches to the biggest value of 0.41 mmol/g at nearly pH value of 8, but the adsorption capacity decreases gradually with the increment of pH values. The figure shows that the absorption capacity of sheath-core bicomponent composite ion exchange fibers for Cu^{2+} is also much too lower at the small pH value (pH = 4), which increases much more quickly with the increment of pH values and reaches to the biggest value of 0.50 mmol/g at nearly pH value of 9, but the adsorption capacity decreases quickly with the increment of pH values. This is because that the unoccupied molecular orbits of both metal ion and hydrion can easily accept lone electron pair of sulfur, but the competition ability of hydrion is stronger than that of metal ion at the small pH values, so that sulfonic groups are not easy to coordinate with metal ions. The suitable pH scope is 7-9, but beyond the scope, the metal ions may be disadvantage in adsorption because of its hydrolysis.

Effect of Initial Concentration on Adsorption Capacity: Keep the total solution volume for the 40 mL, keep the adsorption temperature for 15 °C and keep the same adsorption time for 4 h, while adjust the solution to the best adsorption pH value for Zn^{2+}, Cu^{2+} using the pH buffer solution measured, the adsorption capacity are measured respectively with different initial concentration.

The variations of absorption capacity for Zn^{2+}, Cu^{2+} with different initial concentration are shown in Figure 14. We can see from the figure that the initial concentration has great influence on adsorption capacity of sheath-core bicomponent composite ion exchange fibers for Zn^{2+}, Cu^{2+}, the adsorption capacities are increasing gradually with the increment of initial concentration. The fibers obtained still have bigger adsorption capacity on metal ion with the lower concentration (0.02-0.05 mol/L), it implies that the fibers obtained still have practical application value with the lower concentration.

The curves are fitted from data in Figure 14 based on Langmuir and Freundlich adsorption isothermal equation of the simulation solution in common use, which are usually described in the following forms:

$$C/Q = C/Q_m + 1/Q_m b$$
$$\lg Q = 1\lg C/n + \lg k$$

Where Q represents adsorption capacity (mmol/g), C represents concentration at equilibrium time (mol/L); Q_m represents saturated adsorption capacity (mmol/g); b represents adsorption equilibrium coefficient, meaning high and low adsorption ability of the fibers obtained on metal ions; k, $1/n$ represents Freundlich coefficients respectively. The plots at the given time from the experiment are shown in Figure 3 and Figure 4 respectively. The plots of the given concentrations from the experiment are shown in Figures 15, 16, 17, and 18, respectively.

It is clear from the above diagrams that all the isothermal

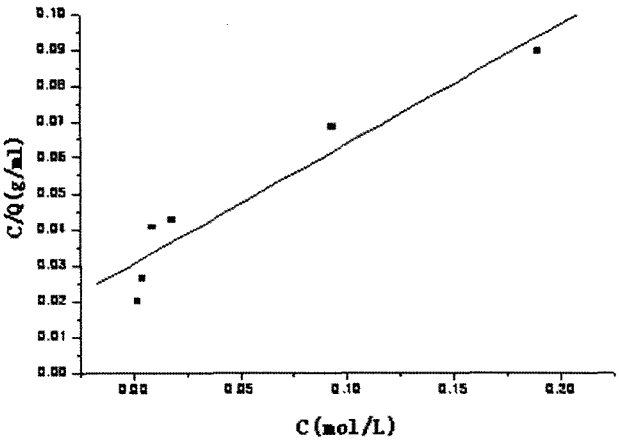

Figure 15. Langmuir isothermal curve of adsorption for Zn^{2+}.

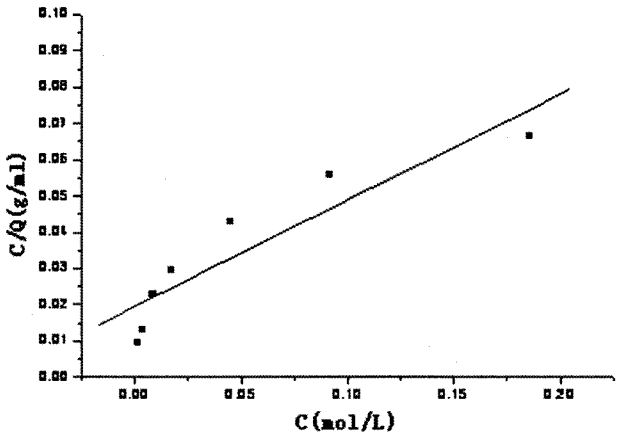

Figure 16. Langmuir isothermal curve of adsorption for Cu^{2+}.

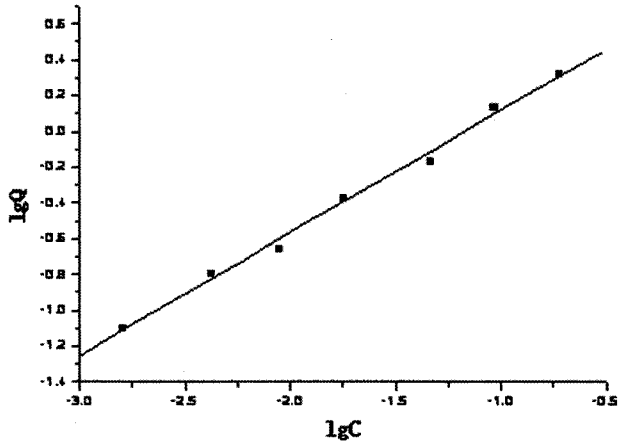

Figure 17. Freundlich isothermal curve of adsorption for Zn^{2+}.

curves of adsorption for Zn^{2+}, Cu^{2+} show the better straight lines within the scope of concentration in the experiment, explaining that the adsorption for metal ion belongs to monolayer adsorption,[18] the process of isothermal absorption can be described by Langmuir and Freundlich adsorption isothermal equation. As shown as Figures 15, 16, 17, and 18, respectively, and the parameters of Q_m, b, $1/n$ and k are obtained respectively by the linear regression, the results are listed in Table II.

The parameter b in Table II displays that adsorption ability of the fibers obtained on Cu^{2+} is bigger than that of Zn^{2+}; the biggest adsorption capacity (Q) of the fibers obtained on Zn^{2+}, Cu^{2+} is close to the saturated adsorption capacity (Q_m) of that within the scope of concentration in the experiment, it implies that the utilization of function groups on the fibers is much higher and is close to theoretical value on the process of adsorption for metal ion; the parameter $1/n$ means difficulty coefficient of reaction,[19,20] it is very difficulty to carry on for the chemical reaction above 2 and very easy to do at 0.1-0.5, as showed in Table II, the values are at 0.5-0.7, explaining that the adsorption reaction for Zn^{2+}, Cu^{2+} is much easier to carry on in the dynamics.

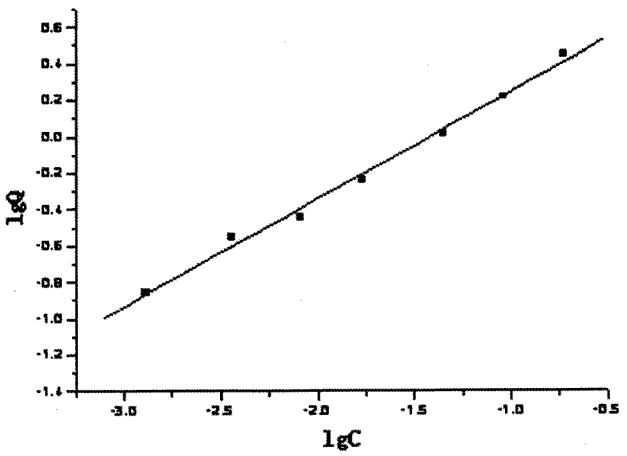

Figure 18. Freundlich isothermal curve of adsorption for Cu^{2+}.

Table II. The Parameters of Langmuir and Freundlich Equations

Metal Ions	Q_m	b	$1/n$	k
Zn^{2+}	2.9968	10.9984	0.6840	6.3200
Cu^{2+}	3.4173	14.9913	0.5879	6.7905

Elution and Regeneration Performance of Fibers. The ion exchange fiber is a new type of chemistry adsorption material, a great deal of experiment data shows that their aggregation structure and morphology have great influence on mechanical strength and adsorption dynamics etc.

Figures 19-22, are SEM images (magnify 2,400 diameters) of the sheath-core bicomponent composite fiber, fiber cross-linked for 4 h, fiber sulphonated for 2 h and fiber exchange with Zn^{2+} respectively. The Figure 20 compared with the Figure 19, the cross-linkage fiber has the very shallow scratches and bulges on the surface, their morphology

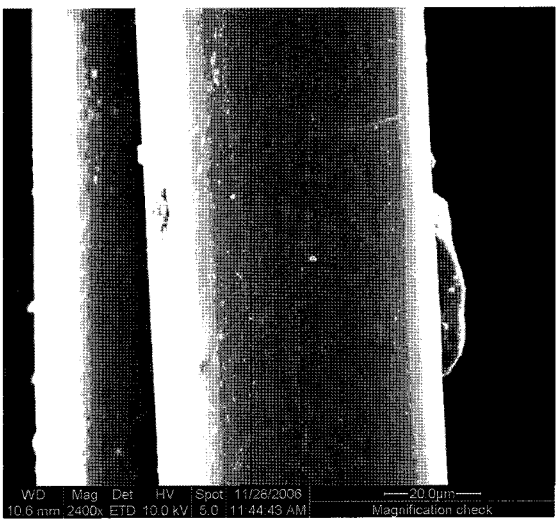

Figure 19. SEM image of the sheath-core bicomponent composite fiber.

Table III. Elution and Regeneration Performance of Fibers

Regeneration Times	Adsorption Capacity for Zn^{2+} (mmol/g)	Regeneration Rate
New Products	0.39	—
1	0.39	100%
2	0.39	100%
3	0.38	97.4%
4	0.37	94.9%
5	0.36	92.3%

are not different from original fiber, and the fiber obtained keep good mechanical function. Figure 21 compared with Figure 19, the fiber morphology changes greatly: Its surface is much rougher than original fiber, appears obvious scratches, the trenches on the surface broaden and deepen, the fiber diameter enlarge, too. The phenomenon above explains that parts of the fibers are dissolved in the reaction so that it damages to the structure of fibers. The phenomenon is showed that sulphonation has an important part in the reaction, which impacts on mechanical function greatly. The Figure 22 compared with the Figure 19, rough spots appear on the surface of fibers and do not appear crushing, crack, deformation etc, which explains that the fibers have good stability in use to make the fibers obtained practical value.

The adsorbed Zn^{2+} by the fibers can be taken off using appropriate concentration hydrochloric acid solution, the adsorption capacity and mechanical function of the regeneration fibers vary little, and the results are listed in Table III. The results in Table III indicate that the adsorption capacity of the regeneration fibers vary little, it explains

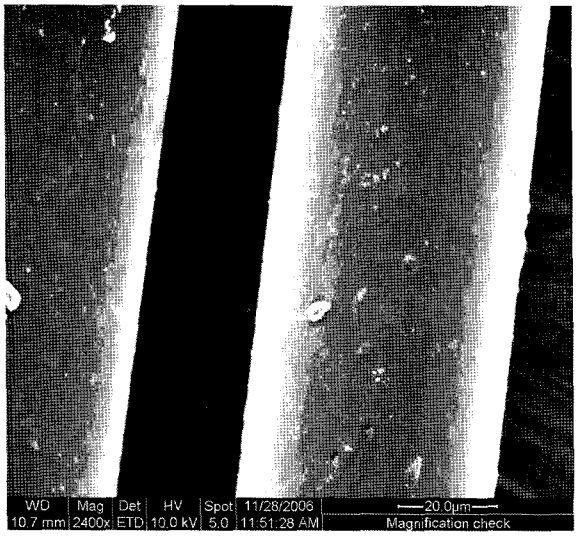

Figure 20. SEM image of the fiber, cross-linked for 4 h.

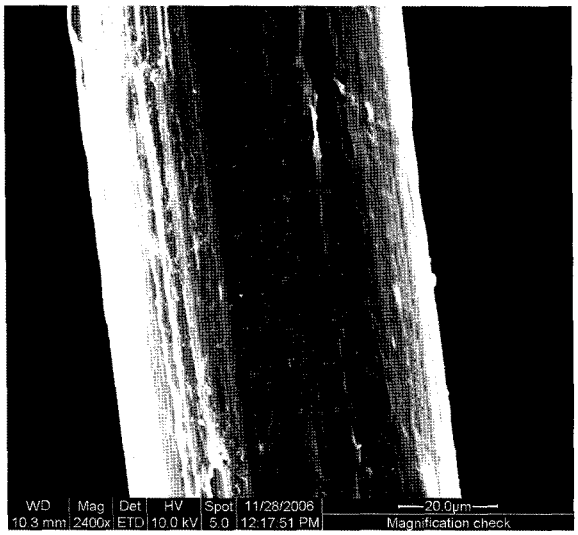

Figure 21. SEM image of the fiber, sulphonated for 2 h.

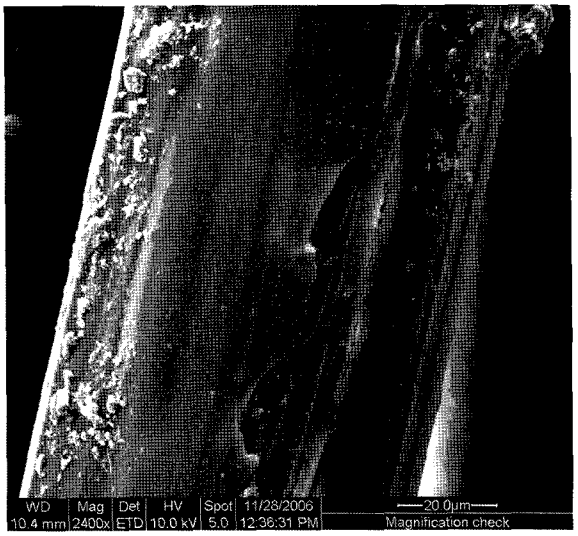

Figure 22. SEM image of the fiber after exchange with Zn^{2+}.

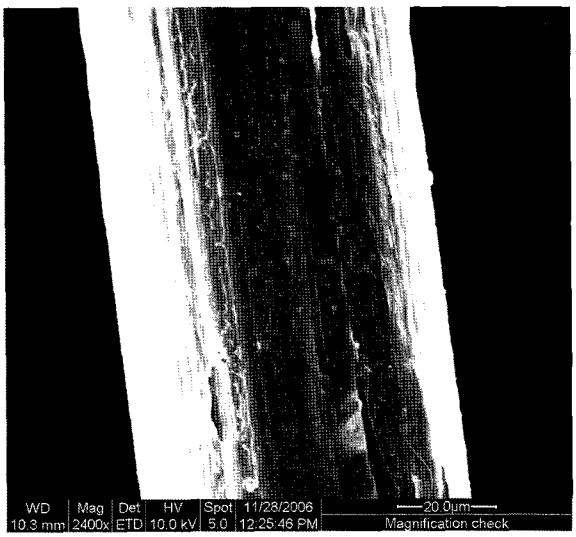

Figure 23. SEM image of the fiber after sorption and desorption circulations for 5 times.

that the function groups on the fibers obtained are stable on the process of sorption and desorption, the regeneration rate reaches to above 92% with sorption and desorption circulations for 5 times.

The SEM image (magnify 2,400 diameters) of sorption and desorption circulations for 5 times is shown in Figure 23, it is clear that the fibers have no obvious variety, do not appear crushing, crack, deformation etc. No residues are left in the exchange-column when the fibers are used for several times, it can effectively avoid the repeated pollution, explaining that the regeneration performance of the fibers obtained are very good, and it can be used for many times.

Conclusions

(1) The optimal technology of making the sheath-core bicomponent composite ion exchange fiber is: 6 g of the fiber, 5 g of $(CH_2O)n$, H_2SO_4(98%) 150 mL, CH_3COOH 25 mL, $C_2H_4Cl_2$ 7.5 mL, and cross-linked at 60 °C for 4 h, sulphonated at 85 °C for 2 h. we gained the cation exchange fibers with better mechanical property and higher exchange capability.

(2) The sheath-core bicomponent composite ion exchange fibers have good adsorptions on metal ion in aqueous solution, the maximal adsorption capacities for metal ions of Cu^{2+}, Zn^{2+} exceed 2 mmol/g, and it can be used timeless. This fiber is suitable for leaching the deleterious ions. And it has good practicability.

(3) The sheath-core bicomponent composite ion exchange fibers obtained have faster absorption rate for Zn^{2+}, Cu^{2+}, the absorption capacity can reach to half of equilibrium capacity in 30 min. Liquid film diffusion is mainly controlling step, the adsorption rate coefficient of Cu^{2+} is bigger than that of Zn^{2+}.

(4) The best adsorption pH value for Zn^{2+} is at nearly pH value of 8; the absorption capacity for Cu^{2+} is much too lower at the small pH value (pH = 4), which reaches to the biggest value at nearly pH value of 9.

(5) The adsorption capacities are increasing gradually with the increment of initial concentration under the condition of constant temperature for 15 °C and the scope of concentration (0.005-0.2 mol/L), all the isothermal curves of adsorption for Zn^{2+}, Cu^{2+} show the better straight lines, explaining that the adsorption for metal ions belongs to monolayer adsorption, the process of isothermal absorption can be described by Langmuir and Freundlich adsorption isothermal equation. The utilization of function groups on the fibers is much higher and is close to theoretical value on the process of adsorption for metal ions; the values of $1/n$ are at 0.5-0.7, explaining that the adsorption reaction for Zn^{2+}, Cu^{2+} is much easier to carry on in the dynamics; adsorption ability of the fibers obtained on Cu^{2+} is bigger than that of Zn^{2+}.

(6) The sheath-core bicomponent composite ion exchange fibers obtained have good chemistry stability and good regeneration performance, which can be used for many times; the regeneration rate reaches to above 92% with sorption and desorption circulations for 5 times, the fibers have no obvious variety, do not appear crushing, crack, deformation etc, explaining the fibers keep good morphology.

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