Amidoxime-Group-Containing Adsorbents for Metal Ions Synthesized by Radiation-Induced Grafting

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Synopsis

Amidoxime-group-containing fibrous adsorbents for metal ions were synthesized by radiation-induced grafting of acrylonitrile followed by amidoximation of cyano groups with hydroxylamine. The degree of amidoximation and the distribution of amidoxime groups in the fiber were follwed by means of electron probe X-ray microanalysis. The efficiency of adsorbing metal ions was increased by alkaline treatment of the adsorbent at high temperature for a short period before use. The order of adsorption for various bivalent metal ions was Hg > Cu > Ni > Co > Cd. From the distribution pattern of metal ions in the fibrous adsorbent, the adsorption was found to be controlled by the diffusion of the solution containing metal ions inside the adsorbent. It was found that confining amidoxime groups superficially and making short chain length of grafts were effective to obtain a high degree of adsorption.

INTRODUCTION

A variety of adsorbents for recovering metal ions dissolved in water or seawater has been reported.[1-8] Especially, adsorbents containing amidoxime groups which make chelate complexes with uranyl ions are noted for the recovery of uranium from seawater.[9-12]

These amidoxime-group-containing adsorbents are synthesized through the reaction of acrylic resins and hydroxylamine. The amidoximation, however, often causes a dimensional instability of the resin when used in aqueous solution because of large swelling in water.[13] When the acrylic resin is made from a copolymer of acrylonitrile and a crosslinking monomer such as divinylbenzene to reduce the swelling, on the other hand, the ability to adsorb metal ions decreases tremendously.[14] One of the causes is the decrease in the free movement of amidoxime groups due to the crosslinking among polymer chains. Therefore, both the stability to swelling and the free movement of the functional groups are essential to the adsorbent which is used in water.

The radiation-induced grafting is known as a method for introducing functional groups in a variety of polymers and inorganic substances.[15] As polymer chains containing functional groups are chemically bonded with trunk polymers only at their chain end, a free movement of the polymer chains is maintained by this method. When a hydrophobic polymer is used as a trunk polymer, the part swollen in water can be restricted only to graft chains. Therefore, the two essential conditions mentioned above are satisfied by this synthesizing method. In addition, the distribution of the introduced functional groups is easily controlled by selecting reaction

conditions such as irradiation dose, dose rate, temperature, and reaction time. However, the studies of synthesizing adsorbents for metal ions by radiation-induced grafting have been little reported.

In the present study, fibrous adsorbents containing amidoxime groups were synthesized by the radiation-induced grafting of acrylonitrile onto fibers and adsorption of heavy metal ions such as copper ions were attempted.

EXPERIMENTAL

Fibers used for synthesizing adsorbents are listed in Table I. The fiber (ca. 40 μm in diameter, and 15mm long) rinsed with acetone and dried in a vacuum oven for 16 h was packed in a polyethylene bag under nitrogen atmosphere and was irradiated wtih an electron accelerator (Dynamitron, Model IEA 3000-25-2, Radiation Dynamics) operating at beam energy of 1.5 MeV and a current of 1 mA at room temperature. In order to reduce the heat accumulation on the sample along with the irradiation, the polyethylene bag was conveyed back and forth under the window of the accelerator at a rate 2.3 m/min. The dose rate was 1 Mrad/pass.

The irradiated fiber was installed in a glass ampoule and was evacuated for 5 min followed by the introduction of purified acrylonitrile under a nitrogen atmosphere. The graft polymerization was carried out at 25°C. When acrylonitrile was grafted in vapor phase, the fiber was separated from liquid acrylonitrile with a perforated plate. After the grafting, homopolymer and unreacted monomer were extracted with N,N-dimethyl formamide. The grafting yield was obtained from the weight increase based on the initial weight.

The amidoxime group-containing fiber (AO fiber) was obtained by heating grafted fiber with 3% hydroxylamine solution (methanol/water = 1/1) at pH 7 then rinsed with methanol and dried at 40°C under a reduced pressure. The amount of amidoxime groups was measured by elemental analysis.

The distribution of amidoxime groups combined with metals in the cross section of AO fiber was measured by means of a JEOL electron probe X-ray microanalyzer (EPMA), Model JXA 733.

About 0.5 g of AO fiber was immersed in 1 L of metal ion (0.1–0.2 mM)-containing Clark-Lubs buffer solution in the pH 2–7 region at 30°C for the prescribed periods. Then the fiber was rinsed with water and was dried in a vacuum oven. A concentrated sulfuric acid was added to a platinum

TABLE I
Fibers Used for Synthesizing Adsorbents

No.	Materials	Producers
1	Tetrafluoroethylene–ethylene copolymer [poly(TFE–E)]	Asahi Glass
2	Polypropylene (PP)	Ube Industries
3	Polyamide	Teijin
4	Polyethylene (PE)	Mitsui Petrochem.
5	Polyester	Teijin
6	Carbon fiber	Toray

crucible containing the fiber and was evaporated to dryness. This procedure was repeated three times. Sodium carbonate was added to the ash of fiber, which was calcined at 550°C and melted. Then $1N$ hydrochloric acid was added to dissolve the melt. The amount of metal in the hydrochloric acid solution was measured by means of a Jarrell-Ash atomic absorption spectrophotometer, Model AA-845.

RESULTS AND DISCUSSION

Grafting

Grafting of acrylonitrile was attempted onto the preirradiated fibrous raw materials as shown in Table I. Figure 1 shows the grafting yield at different reaction time. A relatively high grafting yield was obtained with poly(TFE–E), PP, and polyamide. Especially, the grafting yield with poly(TFE–E) reached ca. 60% in 24 h. The grafting yield with PE, polyester, and carbon fiber, on the other hand, was less than 5%, which is probably due to the low radical concentration in these irradiated polymers. From the results in Fig. 1, the following study was carried out mainly with poly(TFE–E). Moreover, it has a high heat stability and a sufficient resistance to chemical reagents such as base and acid solution due to C—F bonds in polymer structure.

Figure 2(a) shows the effect of diameter of poly(TFE–E) fiber on the grafting yield. The smaller the diameter, the higher the grafting yield. The rate of grafting obtained from Figure 2(a) was found to have a simple relationship with specific surface area of the fiber which was calculated from the fiber diameter as shown in Figure 2(b). These results are due to the fact that grafting is controlled by the diffusion of monomer into the fiber.[16]

As shown in Figure 3, both the grafting rate R_p and the final grafting yield G_f increase with the increase in the irradiation dose D. If the polymer radical is produced in proportion to the nth power of D, that is, [R ·]
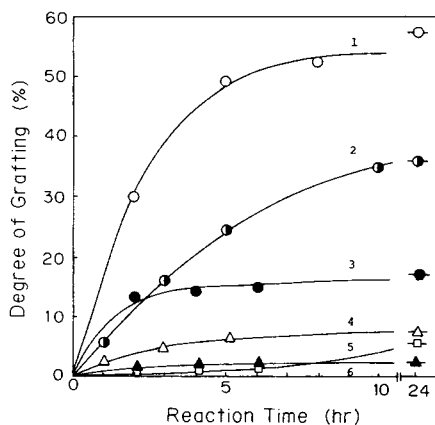

Fig. 1.   Grafting yield of acrylonitrile onto preirradiated fibrous materials. The numbers are the same as shown in Table I.

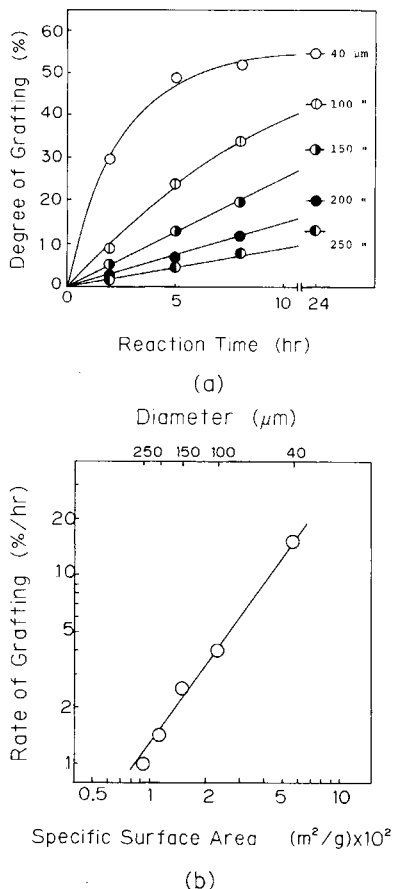Fig. 2.   Effect of diameter of poly(TFE–E) fiber on (a) grafting yield and (b) rate of grafting. (a): (○) 40 μm; (◑) 100 μm; (◐) 150 μm; (●) 200 μm; (◖) 250 μm.

$= k_i D^n$, where [R ·] is the radical concentration and k_i is the rate constant for initiation, respectively, R_p is expressed as

$$R_p = k_p[\text{R} \cdot] \ [\text{M}] = k_i k_p D^n[\text{M}] \tag{1}$$

where k_p is the rate constant for the propagation and [M] is the monomer concentration in the reaction site, respectively. The final grafting yield G_f at $t = t_f$ is obtained by integrating eq. (1) from $t = 0$ to $t = t_f$:

$$G_f = \int_0^{t_f} R_p \, dt = k_i k_p D^n[\text{M}]t_f \tag{2}$$

Equations (1) and (2) show that both R_p and G_f are proportional to D^n. From the results in Figure 3, n is estimated as ca. 0.5. The result that R_p is proportional to $D^{1/2}$ agrees with the previous work in which styrene was grafted onto the preirradiated TFE Teflon.[17]

From the dependency of grafting rate on the reaction temperature the apparent activation energy was estimated as ca. 13 kcal/mol, which is
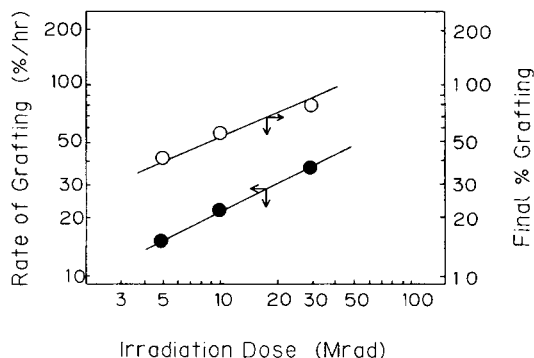
Fig. 3. Effect of irradiation dose on rate of grafting (●) and final grafting yield (○).

comparable to the previously reported values for a variety of radiation-induced grafting.[18]

Amidoximation

As shown in the experimental section, AO fiber was obtained by converting cyano groups of graft chains to amidoxime groups. Figure 4 shows the effect of temperature on the amidoximation of the grafted fiber with average degree of grafting: 54–58%. At 40°C the conversion after 10 h was still less than 5%. The temperature was raised until it reached the boiling point of hydroxylamine solution (ca. 80°C). The conversion reached more than 60% after 6 h. The activation energy for amidoximation was estimated as 12 kcal/mol from the Arrhenius plots of the conversion as shown in Figure 4.

The distribution of the amidoxime groups in the cross section of AO fiber was measured by means of EPMA. Figure 5 shows the distribution of amidoxime groups when the period of amidoximation was changed from 1 to 6 h at 80°C. It is clear that the amidoximation gradually proceeds from the surface to the center of the fiber and that it takes more than 6 h to obtain a homogeneous distribution.
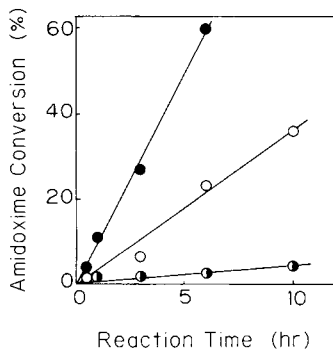

Fig. 4. Effect of temperature on amidoximation of the grafted poly(TFE–E) fiber (grafting yield = 54–58%): (◐) 40°C; (○) 60°C; (●) 80°C.
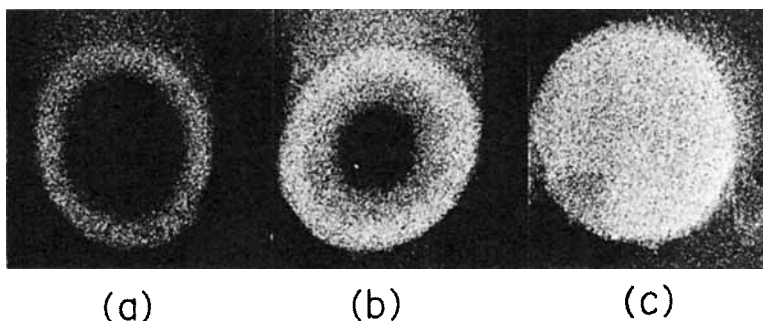
(a)   (b)   (c)

Fig. 5.   Distribution of amidoxime groups in the cross section of AO fiber measured by means of EPMA; reaction time (h): 1; (b) 3; (c) 6.

Figure 6 shows the temperature effect on the width of distribution of amidoxime groups in AO fiber obtained from EPMA measurement. When the temperature is high and the reaction time of amidoximation is long, the distribution becomes widespread. The almost linear relationship of the width with reaction time indicates that amidoximation in the center of the fiber proceeds at a similar rate as on the surface region. The activation energy for spreading amidoxime groups in the fiber was estimated as ca. 10 kcal/mol. This value is in fair agreement with the above-mentioned activation energy for converting cyano groups to amidoxime groups.

Such thermodynamic similarity between the conversion of amidoximation and the spread of distribution of amidoxime groups inside the fiber is more clearly indicated when these values are plotted against each other as shown in Figure 7. Clearly, the conversion increases in proportion to the increase in the width under all the present experimental conditions. Therefore, it is reasonable to say that the amidoximation occurs homogeneously at least within 20 μm from the surface of the fiber. Probably, cyano groups of graft chains exist homogeneously in the fiber and as soon as the hydroxylamine solution reaches the cyano groups the amidoximation occurs. In other words, the reaction is controlled by the diffusion of hydroxylamine solution in the fiber.
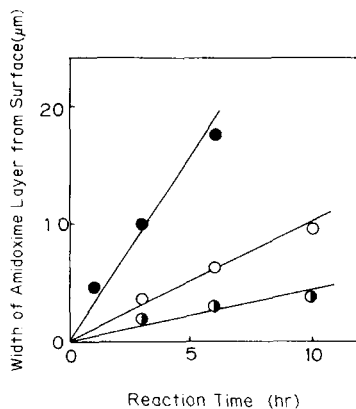

Fig. 6.   Effect of temperature on the width of distribution of amidoxime groups in AO fiber. The symbols are the same as shown in Figure 4.
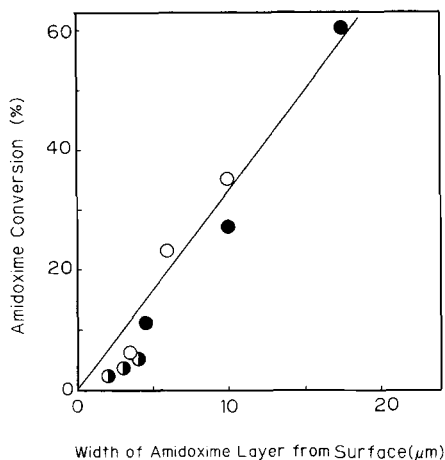
Fig. 7.   Relationship between the conversion of amidoximation and the spread of distribution of amidoxime groups. The symbols are the same as shown in Figure 4.

Adsorption of Metal Ions

The dried AO fiber did not adsorb metal ions at room temperature. One of the causes is the insufficient swelling of the fiber in metal ion-containing solution. The hydrophilicity of poly(TFE–E) fiber itself is virtually negligible and amidoxime groups are not so hydrophilic.[10]

Heating of AO fiber in alkaline solutin was found to increase the swelling of AO fiber in aqueous solution. For example, the contact of AO fiber with $0.5N$ potassium hydroxide solution at 20°C for 8 h elicited 30% augmentation in the water uptake.

The increase in hydrophilicity of the fiber is expected to increase the adsorption of metal ions. Figure 8 shows the effect of temperature of alkaline treatment on adsorption efficiency expressed as the percentage of amidoxime groups used for complexation with copper ions. It is clear that raising the temperature increases the efficiency. Although the efficiency abruptly
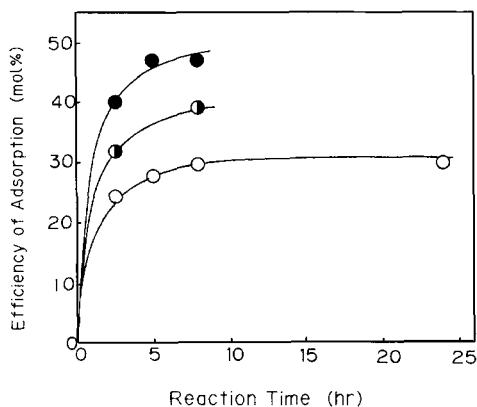

Fig. 8.   Effect of temperature of alkaline treatement of AO fiber on adsorption efficiency for copper ion: (◯) 20°C; (◑) 50°C; (●) 70°C.

increased when the fiber was treated with alkaline solution for a short period, the elongation of treatment period was not so effective to increase the efficiency. As shown in Figure 8, the efficiency levels off when the period is more than 8 h. In addition, the long contact of AO fiber with alkaline solution at high temperature should be avoided to reduce an undesirable decomposition of amidoxime groups.[10] It was found that the treatment at 80°C for 10 min was the optimum condition to keep a high adsorption capacity with less decomposition of amidoxime groups introduced into poly(TFE–E).

When a sufficient period of adsorption was maintained, the adsorption of copper ion increased in proportion to the amount of amidoxime groups in the alkaline treated AO fiber as shown in Figure 9. From the slope, the number of amidoxime groups necessary for fixing one copper ion by complexation was estimated as, on the average, 3.3. As amidoximes are supposed to be bidentate, two amidoximes may be used for chelate formation with a copper ion which makes a square planar chelate. Therefore, the number 3.3 indicates that more than one extra amidoxime which does not directly participate in the chelate formation exists. Probably, the graft chains containing amidoximes have a loop structure, which makes it impossible that some of the amidoximes which exist in the middle of the loop take part in the chelate formation.

Figure 10 shows the effect of acidity of metal ion- containing solution on the adsorption of Hg^{2+}, Cu^{2+}, and Cd^{2+}. About 0.1 mmol of Hg^{2+} was adsorbed per 1 gAO fiber at pH 2, while no adsorption of Cu^{2+} and Cd^{2+} was observed at this acidity. Cd^{2+} was not adsorbed until pH was beyond 4.

The amount of adsorbed metal ions increased with the increase in pH value. A steep increase was observed in the case of Hg^{2+} and Cu^{2+} when pH was more than 5. However, when pH was beyond 6 a precipitation of Cu was observed. The order of adsorbing various bivalent metal ions was

$$Hg > Cu > Ni > Co > Cd$$

which agrees with Irving–Williams order.[19]

Figure 11 shows the distribution of copper ions complexed with amidoxime groups at various contact periods. It is apparent that the migration of
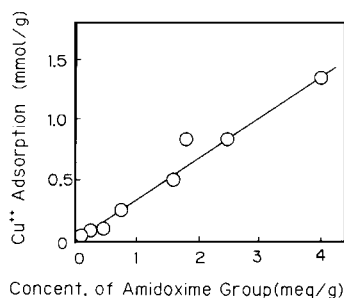

Fig. 9.   Relationship between the amount of amidoxime groups in AO fiber and the amount of adsorbed copper ions.
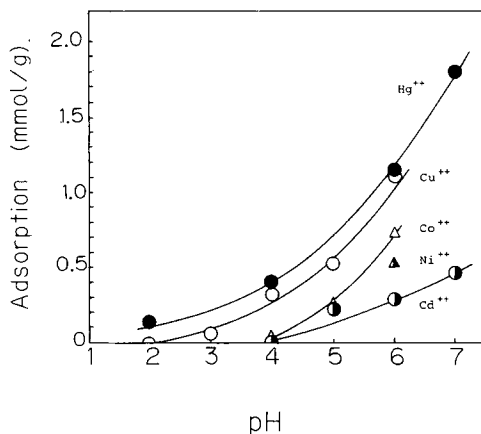
Fig. 10. Effect of acidity of metal ion-containing solution on the adsorption of various bivalent metal ions.

copper ion through the amidoxime group layer is slow. It took about 1 day to obtain an almost homogeneous distribution of copper ions in AO fiber. The rapid increase in the population of copper ions on the surface region, on the other hand, suggests that confining amidoxime groups superficially on the adsorbent fiber is effective to obtain a high adsorption ability. This assumption was confirmed by the result shown in Figure 12 where the distribution of amidoxime groups in AO fiber and the adsorption amount
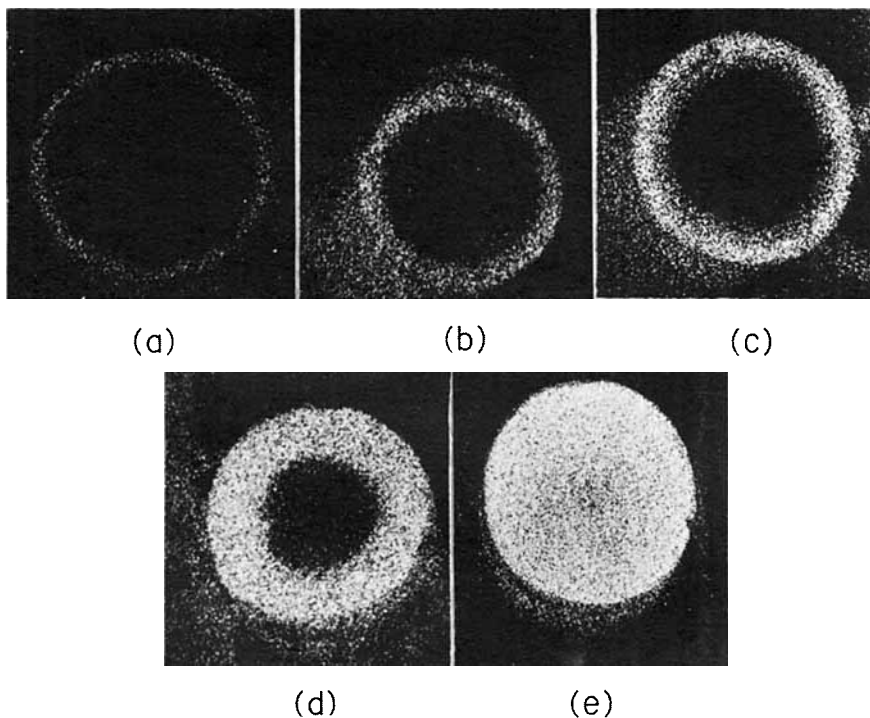

Fig. 11. Distribution of copper ions complexed with amidoxime groups at various contact periods: (a) 1 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 24 h.
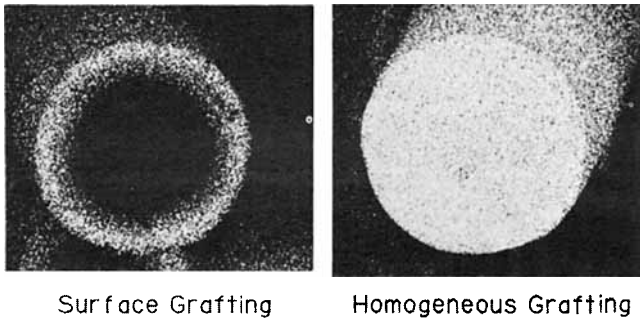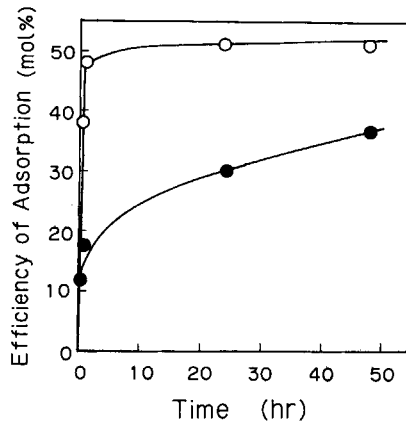
Fig. 12. Distribution of amidoxime groups and adsorption amount of copper ions with the adsorbents made by (○) surface grafting and by (●) homogeneous grafting.

of copper ions were compared between two types of adsorbents—one made by surface grafting with acrylonitrile vapor and the other by homogeneous grafting using liquid acrylonitrile. It is clear that amidoxime groups in the surface layer (within 10 μm from the surface) provide about twice as much adsorption of copper ions as the homogeneously distributed amidoximes do.

Another possibility of obtaining high adsorption ability is shown in Figure 13, where AO fibers with similar grafting yield and therefore an almost constant amidoxime amount obtained at different irradiation doses were
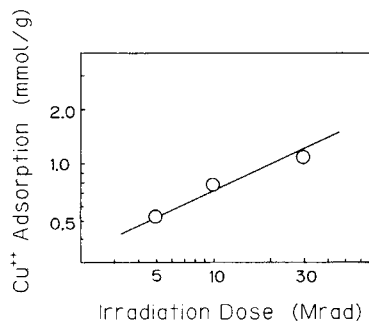

Fig. 13. Effect of irradiation dose for grafting acrylonitrile on adsorption of copper ions.

used. By increasing the irradiation dose, the number of trunk polymer radicals which can initiate graft polymerization increases. As the grafting yield is the product of the number of initiation radicals and the length of the graft chains, the result that these AO fibers have similar grafting yield indicates that the graft chain lengths are different according to the difference in the number of initiation radicals. It is clear that the AO fiber of shorter chain length (or irradiated with higher dose) provides a higher adsorption capacity for copper ions. Probably, the shorter chains have more flexibility of the movement of amidoxime groups for the complex formation with copper ions.

AO fiber has high stability to various kinds of treatment. For example, when dry AO fiber was treated with 2.5% potassium hydroxide solution at 80°C for 10 min, the diameter increased only 4%, which proves that AO fiber swells little in alkaline solution. No further increase in diameter was observed when the alkaline treated AO fiber was contacted with water at 30°C for 24 h, while a considerable amount of water uptake (ca. 30%) was observed as mentioned above.

Thus, this new adsorbent produced by radiation-induced grafting proves very effective for the use in water because of high adsorption ability for heavy metal ions and sufficient stability under various conditions.

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