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# A New Type of Amidoxime-Group-Containing Adsorbent for the Recovery of Uranium from Seawater. III. Recycle Use of Adsorbent

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## Abstract

An amidoxime-group-containing adsorbent for recovering uranium from seawater was made by radiation-induced graft polymerization of acrylonitrile onto polymeric fiber, followed by amidoximation. Uranium adsorption of the adsorbent contacted with seawater in a column increased with the increase in flow rate, then leveled off. The relationship between uranium adsorption in a batch process and the ratio of the amount of seawater to that of adsorbent was found to be effective in evaluating adsorbent contacted with any amount of seawater. The conditioning of the adsorbent with an alkaline solution at higher temperature (~80°C) after the acid desorption recovered the adsorption ability to the original level. This made it possible to apply the adsorbent to recycle use. On the other hand, the adsorbent conditioned at room temperature or that without conditioning lost adsorption ability during recycle use. The increase in water uptake was observed as one of the physical changes produced during recycle use of the alkaline-conditioned adsorbent, while the decrease in water uptake was observed with the unconditioned adsorbent. The IR spectra of the adsorbent showed a probability of reactions of amidoxime groups with acid and alkaline solutions, which can explain the change in uranium adsorption during the adsorption-desorption cycle.

## INTRODUCTION

The recovery of uranium from seawater has been noted as one of the useful techniques for supplying uranium in the future. The process using adsorbents is thought to be the most effective methods for recovering

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uranium because of the high selectivity for uranium, the ease of handling, the safety to the environment, etc. Among many types of adsorbents, an amidoxime-group-containing adsorbent has widely been studied (*1–7*). This is mainly due to its large adsorption of uranium and a high stability to chemical reagents like acids used for desorption when compared with such inorganic adsorbents as hydrous titanium oxide.

In our previous papers (*6–8*) a new method for producing a chemically stable adsorbent containing amidoxime groups was proposed. The characteristics of the method are (a) the ease of controlling the amount of amidoxime groups in the adsorbent, (b) the probability of providing a synergistic effect on uranium adsorption by mixing plural functional groups, and (c) the availability of chemically stable polymers as trunk polymers of adsorbents. The uptake of uranium in 10 d with the adsorbent was ~200 μg/g, which is comparable to or higher than the uptake with the previously reported amidoxime-group-containing adsorbents (*3*).

In any future practical plants for uranium recovery from seawater, a large amount of adsorbents will be used. The exchange of adsorbent in a complicated and huge plant is tedious work. In addition, minimizing the adsorbent amount is important from the economical point of view. Therefore, it is desirable to use adsorbents repeatedly. The adsorbents should be stable to recycle use.

The purpose of the present paper is to estimate the adsorption ability of the newly developed adsorbent in recycle use and to clarify the factors that determine the durability of the adsorbent.

## EXPERIMENTAL

The adsorbent was synthesized by radiation-induced grafting of acrylonitrile onto tetrafluoroethylene–ethylene copolymer, followed by the conversion of cyano groups of graft chains to amidoxime groups with hydroxylamine. The details of the procedure were reported in previous papers (*6–8*). The adsorbent was conditioned with a 2.5% KOH solution (methanol–water mixture in the ratio 3:1) at 80°C for 10 min before use.

The adsorption of uranium from seawater was carried out with (a) a batch process (the volume of the vessel = 2 L), (b) a semibatch process (5 L seawater was intermittently exchanged of fresh seawater), and (c) a flow process (two columns: 1 cmϕ × 10 cmH and 10 cmϕ × 50 cmH). The desorption of uranium from the adsorbent was accomplished by contacting the adsorbent with 1 *N* hydrochloric acid for 1 h at 25°C. The amount of uranium in the acid extract, which was complexed with Arsenazo III, was measured optically at 665 nm by means of a Shimadzu spectrophotometer, model UV 100-02. The amounts of alkaline earths in the acid extract from the adsorbent were determined by means of a Jarrell-Ash atomic absorption and flame emission spectrophotometer, model AA-8200. The infrared spectra were measured with a JASCO diffraction grating infrared spectrophotometer, model A-302. The water uptake of the adsorbent was determined by the difference in weight between the wet condition (the sample, immersed in water, stood above the container of water for 24 h) and the dry condition (the sample was dried in a vacuum oven).

## RESULTS AND DISCUSSION

Because the adsorption of uranium with a column is controlled by such operating conditions as the flow rate of seawater and the amount of adsorbent, the adsorption ability of the adsorbent was estimated by changing the flow rate and the amount of adsorbent in two columns of different sizes. Figure 1 shows the adsorption amount of uranium obtained by the large column. Uranium adsorption increased with an increase in flow rate from 0.3 to 1.5 kL/d. As shown in Fig. 2, however, the amount of uranium adsorbed in 10 d is not a linear function of flow rate. The amount gradually levels off and finally no increase is observed when the flow rate is more than 2 kL/d in the large column and 5 L/d in the small column.

This saturation of adsorption is correlated with the adsorption mechanism. When the flow rate becomes large, the diffusion of the bulky uranium tricarbonate anion in the adsorbent cannot follow the flow rate. In other words, the diffusion becomes the rate-determining step. Because the present adsorbent is made by embedding amidoxime groups in a hydrophobic trunk polymer, the diffusion of uranyl tricarbonate anion, which is the main form of uranium in seawater, is probably slow. The previous results that the co-introduction of such a hydrophilic group as carboxyl along with amidoxime group improves the adsorption (7) support the probability of diffusion control of ions in adsorbents.

As shown in Fig. 2, the flow rate at saturation of adsorption obtained with the large column is quite different from that obtained in the small one. This result suggests that the scale-up effect exists in the adsorption process. That is, saturation in the small column occurs at a smaller flow rate compared to the large column. This difference, however, should be considered along with the amount of adsorbent packed in each column.

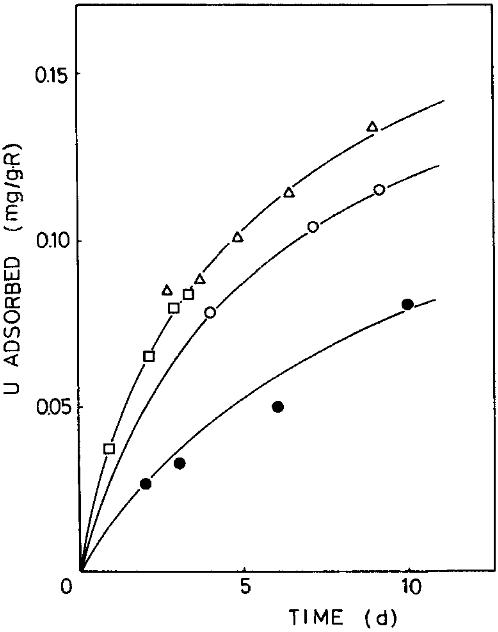


FIG. 1. Effect of flow rate of seawater in column on adsorption of uranium: (●) 0.3, (○) 1.0, (△) 1.5, and (□) 3.0 kL/d.

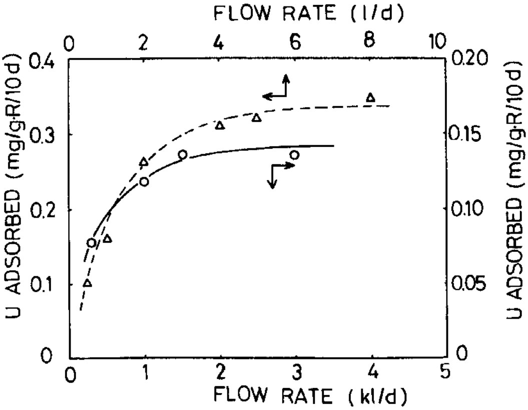


FIG. 2. Relationship between adsorption of uranium in 10 d and flow rate of seawater: (○) large column and (△) small column.

When the large column contained 40 g of the adsorbent, saturation occurred at 2 kL/d, while when the small column contained 0.1 g of the adsorbent, saturation was at 5 L/d. When the ratio of the flow rate at saturation of adsorption to the amount of adsorbent is calculated, both columns happen to give a similar value, 50 L/g/d. This result suggests that the adsorption obtained in columns of different sizes can be compared with each other at the same ratio of the flow rate of seawater to the amount of the adsorbent.

The ratio of the amount of seawater to that of the adsorbent is important in the batch process too. Uranium adsorption was studied with the batch process by changing the amount of seawater from 2 to 10 L and that of the adsorbent from 0.1 to 1 g. Although Fig. 3 shows some scatter, the amount of adsorbed uranium increases with an increase in the ratio of the amount of seawater to that of adsorbent (liquid–solid ratio).

Batch process is often used to estimate the adsorption ability of adsorbents (*9*). However, comparison of adsorption ability among different adsorbents has rarely been made. One of the reasons is the difficulty of comparing the ability when the amount of seawater or that of adsorbent, or both, are different. It is proposed that evaluation of the ability of fibrous adsorbents should be carried out by a batch process containing 10 L seawater and 1 mL adsorbent with agitation (*10*). However, a decision on the experimental size is not always necessary. The results in Fig. 3 indicate that evaluation is possible at any amounts of seawater and/or adsorbent when such a relationship between uranium

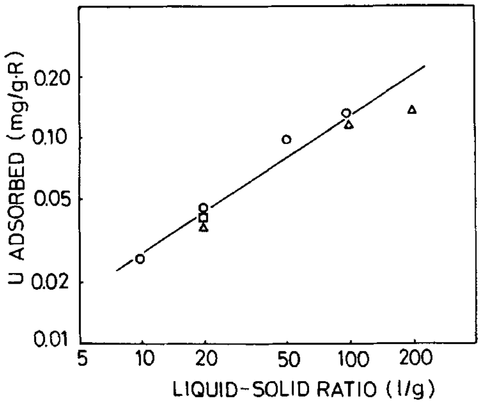


FIG. 3. Relationship between adsorption of uranium and liquid–solid ratio in the batch process: (□) amount of seawater = 2, (○) 5, and (△) 10 L.

adsorption and the ratio of the amount of seawater to that of adsorbent is obtained.

Because the adsorption amount is saturated at higher flow rates, as shown in Fig. 2, it is necessary to use the adsorbent repeatedly in order to obtain a higher deposit of uranium in the adsorbent.

Alkaline conditioning was always employed before the start of adsorption, as mentioned in the Experimental section. Therefore, in the first place, it was studied if conditioning is also necessary at the beginning of each cycle of repeated use. As shown in Fig. 4, uranium adsorption of the adsorbent without alkaline conditioning was virtually zero in 4 day's adsorption, while with the adsorbent conditioned at 80°C it was ~0.11 mg/g · R and with the adsorbent conditioned at room temperature it was ~0.08 mg/g · R. It was rather surprising that the adsorption ability obtained by conditioning at room temperature for 1 week was never equal to that obtained by conditioning at 80°C for only 10 min.

Such a clear difference in the adsorption ability, which was due to different conditionings, was also observed in recycle use. After the first adsorption, the mass of the adsorbent was contacted with acid for desorption and was divided into three groups: I, II, and III. Then Group I was conditioned with alkaline solution at 80°C for 10 min, Group II was

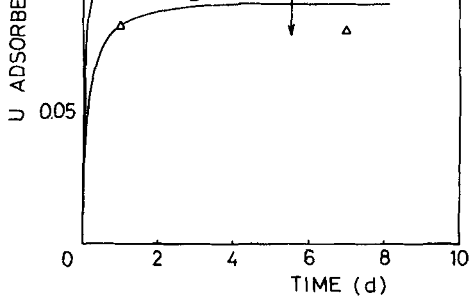


FIG. 4. Effect of alkaline conditioning on uranium adsorption in the semibatch process (exchange of seawater, 5 L/d × 4; adsorbent, 0.25 g): (○) at 80°C and (△) at room temperature.

conditioned at room temperature for 24 h, and Group III was used without conditioning. Figure 5 shows the amount of adsorbed uranium obtained by repeated use of these three types of adsorbents. Although Adsorbents II and III gradually lost their adsorption ability, Adsorbent I maintained its initial adsorption level up to Cycle 5, followed by a gradual decrease. The decrease is, however, much smaller when compared with the decrease with other types of amidoxime-group-containing adsorbents. For example, it was reported that about a 6% decrease was observed at each cycle with a commercially available amidoxime resin (*11*).

Along with the adsorption of uranium, alkaline earth metals were adsorbed during recycle use. As shown in Fig. 6, it was observed that both amounts of adsorbed magnesium and calcium increased with an increase in the number of cycles. Considering the previous work that showed the adsorption of these alkaline earths was promoted by introducing such a hydrophilic functional group as carboxyl to the adsorbent (*7*), the results in Fig. 6 suggest the possibility of the occurrence of physical and chemical changes in the adsorbent which facilitate the adsorption of these alkaline earth metals during the adsorption-desorption cycle.

One of the physical changes of the adsorbent during recycle is the change in water uptake. As shown in Fig. 7, the adsorbent conditioned with alkaline solution at 80°C for 10 min showed an increase in water uptake with an increase in the number of cycles while that without alkaline conditioning showed a decrease in water uptake. This decrease is

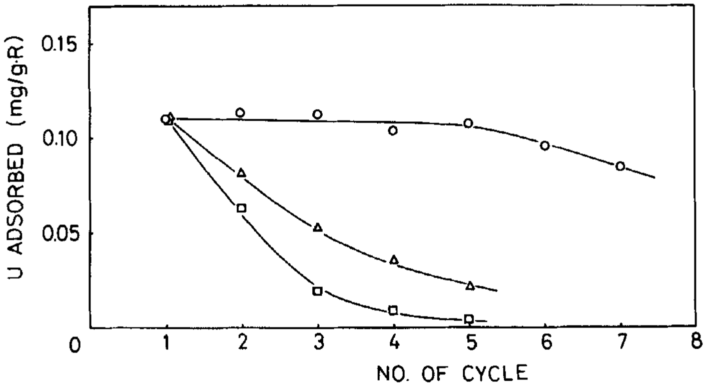


FIG. 5. Amount of uranium adsorbed during recycle use in the semibatch process: (○) conditioned with alkaline solution at 80°C for 10 min after desorption, (△) conditioned at room temperature for 24 h, and (□) without conditioning.

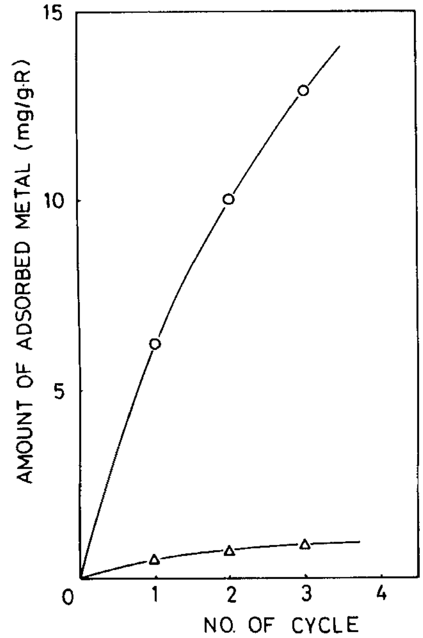


FIG. 6. Amount of alkaline earth metals adsorbed during recycle use in the semibatch process: (O) magnesium and (Δ) calcium.

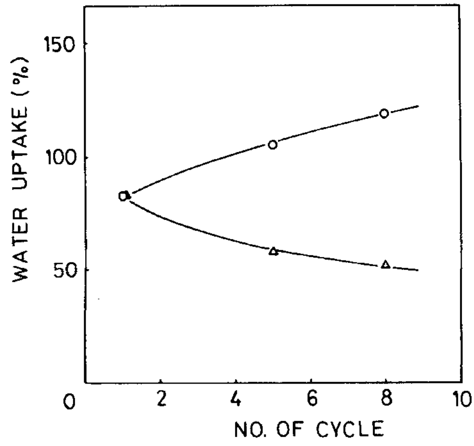


FIG. 7. Effect of recycle use of adsorbent in the semibatch process on water uptake of the adsorbent: (O) conditioned with alkaline solution at 80°C and (Δ) without conditioning.

probably due to acid desorption. That is, contact of the adsorbent with acid brings about shrinkage of the polymer matrix, which disturbs the diffusion of water inside the polymer matrix. A similar shrinkage was observed on amidoximated cotton after acid scouring (*12*). On the other hand, alkaline conditioning at 80°C causes expansion of the spaces among polymer matrices and increases water uptake (*8*).

Chemical change along with recycle use was followed by infrared spectra measurement. Three samples containing amidoxime groups of 1.2, 2.6, and 4.4 meq/g, respectively, were used for the measurement. As a reference, the sample containing poly(acrylonitrile) graft chains before conversion to amidoxime groups was used. The difference in infrared spectra between samples containing amidoxime groups and those containing nitrile groups eliminated strong absorptions due to the $>CH_2$ and $>CF_2$ skeletal structures of the trunk polymer. Figure 8(a) and (b)

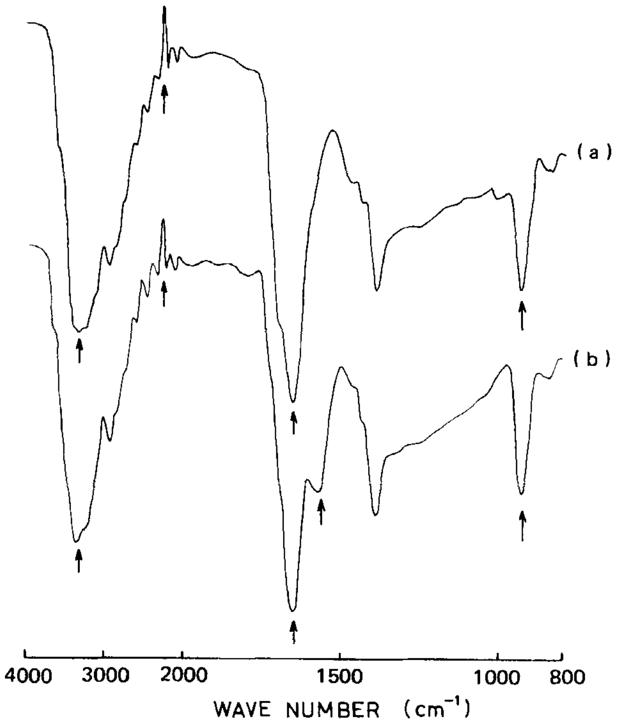
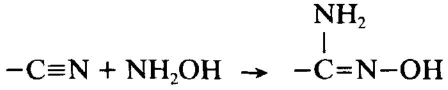


FIG. 8. Infrared spectra of amidoxime-group-containing adsorbent: (a) after desorption with acid and (b) after conditioning with alkaline solution.

show the spectra after desorption with acid and after alkaline conditioning at 80°C, respectively. The main absorptions at 3200–3400, 1650, and 940 $cm^{-1}$ are due to $-OH$, $>C=N-$, and $=N-O-$ of amidoxime groups, respectively (*13*). The decrease in adsorption at 2250 $cm^{-1}$ indicates the consumption of nitrile groups in the amidoximation as follows:



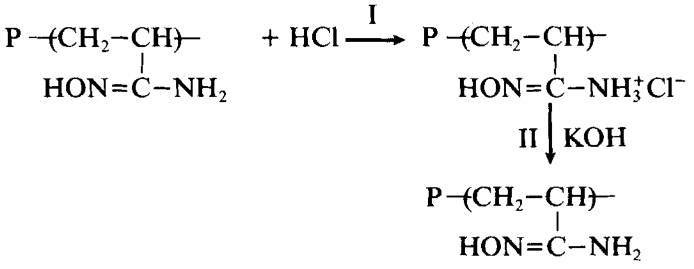
$$-C\equiv N + NH_2OH \rightarrow -\overset{NH_2}{\overset{|}{C}}=N-OH \qquad (1)$$

The absorption at 1580 $cm^{-1}$, which was only observed in the alkaline conditioned sample, is due to bending of $-NH_2$ of the amidoxime group. The disappearance of this absorption in the acid form is due to the reaction of $-NH_2$ with HCl:

$$-NH_2 + HCl \rightarrow -NH_3^+Cl^- \qquad (2)$$

From the spectra shown in Fig. 8, the absorbance at 930 $cm^{-1}$ ($=N-O-$) was used as an indicator of the change in the amount of amidoxime groups through acid desorption and alkaline conditioning. Figure 9 shows the change in absorbance at 930 $cm^{-1}$ with an increase in the number of cycles. The decrease in the amount of amidoxime groups is estimated to be ~20% at each acid desorption. It is clear that decreased absorbance is virtually recovered by alkaline conditioning up to the 3rd cycle.

These decreases and increases in the amount of amidoxime groups are probably due to the reaction of amidoxime groups with acid and alkaline solutions as follows:



$$\underset{HON=C-NH_2}{P\!-\!(CH_2-\overset{}{CH})\!-} + HCl \xrightarrow{I} \underset{HON=C-NH_3^+Cl^-}{P\!-\!(CH_2-CH)\!-} \xrightarrow[KOH]{II} \underset{HON=C-NH_2}{P\!-\!(CH_2-CH)\!-} \qquad (3)$$

where P = trunk polymer.

Reaction I is the neutralization of a weak base with a strong acid. Reaction II is the reaction between a strong base and a salt obtained from

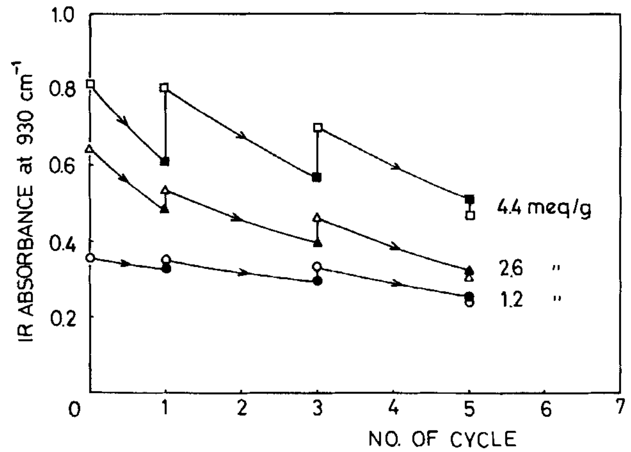
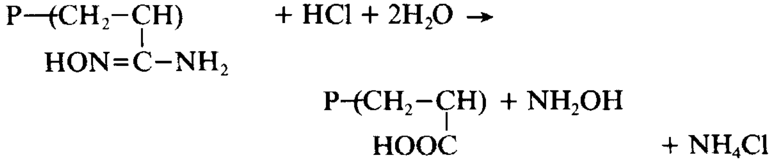


FIG. 9. Change in absorbance at 930 cm$^{-1}$ with an increase in the number of cycles:

| Concentration of amidoxime group (meq/g) | After acid desorption | After alkaline conditioning |
|---|---|---|
| 1.2 | ● | ○ |
| 2.6 | ▲ | △ |
| 4.4 | ■ | □ |

a weak base and a strong acid. That is, the introduction of HCl to the amidoxime groups produces a salt in the form of $-NH_3^+Cl^-$ which does not show the absorption at the position for amidoxime groups (930 cm$^{-1}$) but is converted to the original amidoxime form through contact with KOH. The absorption at 1580 cm$^{-1}$, which is due to the amino group, clearly indicates a conversion such as that indicated in Eq. (3) occurs during the acid desorption-alkaline conditioning cycle.

The result is that recovery becomes almost impossible at the 5th cycle, as shown in Fig. 9, and indicates the possibility of an irreversible reaction either in Step I or II of Eq. (3). A possible reaction is the formation of acid from amidoximes:



$$\underset{\text{HON=C-NH}_2}{\text{P}\!-\!(\text{CH}_2\text{-CH})} + \text{HCl} + 2\text{H}_2\text{O} \rightarrow \underset{\text{HOOC}}{\text{P}\!-\!(\text{CH}_2\text{-CH})} + \text{NH}_2\text{OH} + \text{NH}_4\text{Cl} \qquad (4)$$

This equation shows that the amidoxime produces acid, hydroxylamine, and ammonium salt when it is hydrolyzed with acid. The formation of hydroxylamine through hydrolysis has been confirmed by a polarographic determination (*11*). Therefore, Step I in Reaction (3) and Reaction (4) are competitive in acid desorption. The results in Figs. 5 and 9 indicate that Reaction (4) predominants with repeated use.

By considering the results mentioned above, it is concluded:

(a) The decrease in the adsorption ability of the adsorbents conditioned with alkaline solution at room temperature or those without alkaline conditioning during the adsorption-desorption cycle is due to 1) insufficient recovery of amidoxime groups after desorption and 2) a decrease in water uptake.

(b) The adsorption ability of the adsorbent conditioned with alkaline solution at 80°C is maintained. This may be due to a balance between the increase in water uptake and a decrease in the amount of amidoxime groups.

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