(Received 12 July, 1999 ; Accepted 9 September, 1999)

Sorption of Metal Ions by Bead Cellulose Grafted with Amidoximated Polyacrylonitrile

Nobuyoshi Aoki^{*1}, *Kounosuke Tanaka*^{*2}, *Munenori Sakamoto*^{*3}, and *Ken-ichi Furuhata*^{*2}

^{*1}Molecular Engineering Division, Kanagawa Industrial Technology Research Institute, 705-1, Shimoimaizumi, Ebina-shi, 243-0435, Japan

^{*2}Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

^{*3}College of Education, Joetsu University of Education, Yamayashiki-machi, Joetsu-shi, 943-8512, Japan

Abstract : Bead cellulose samples with amidoximated polyacrylonitrile grafts were examined as sorbents for metal ions. The amount of the ion sorbed from 40 mM solution in a fixed period increased in the order Cd (II), Zn (II) < Pb (II) < Cu (II) << Ag (I). The treatment of bead samples with NaOH solutions caused the swelling, and both the amount of the metal ion sorbed and the sorption rate increased considerably after the NaOH treatment. More than 90% of metal ions sorbed by the beads were desorbed in 0.5 M H₂SO₄. The sorption-desorption-NaOH treatment cycle could be repeated without significant reduction in the extent of sorption.

1. Introduction

The sorption of metal ions from aqueous solutions is important, for example, for the recovery of precious metals from seawater and the exclusion of toxic metals from waste waters, and various chelating resins have been examined for the purpose. Examples are polymers having amidoxime groups which were tested most frequently for the recovery of uranium from seawater [1,2]. Amidoxime compounds form colored complexes with some kinds of metal ions and several of them are used in the quantitative analysis of metals [3].

Amidoxime resins are obtained via the amidoximation of nitrile groups in polymers (for example, polyacrylonitrile) with hydroxylamine. Graft copolymers of acrylonitrile with starch [4] and cellulose [5] were used as sorbents for metal ions after amidoximation. The polysaccharide matrix is considered to have some advantages because it is hydrophilic and biodegradable in nature. The shape of sorbent is important for the sorption performance and

fibrous [6-9] and porous [10,11] samples having high relative surface area were tested.

We reported previously [12] the graft copolymerization of acrylonitrile onto microporous bead cellulose and the amidoximation of polyacrylonitrile grafts. About 40% of the nitrile groups could be converted into amidoxime groups. In this article we describe the sorption of several metal ions by these amidoximated bead cellulose samples. The effect of NaOH treatment on the sorption behavior was studied. These bead samples showed no significant decrease in the performance after repeated sorption-desorption-NaOH treatment cycles.

2. Experimental

2.1 Materials

Samples of bead cellulose (Bellfine; diameter 70–100 μ m; water content 74%) were kindly supplied by Kanebo Co., Ltd. Acrylonitrile was grafted onto bead cellulose at 40°C for 4 h using (NH₄)₂Ce(NO₃)₆ as an initiator and graft copolymers were treated with

hydroxylamine in methanol at 90°C in a pressure bottle as described in the previous paper [12]. Amidoximated bead cellulose (Cell-*g*-PAAmd) samples were washed with water repeatedly, then with acetone and were immersed in acetone for 30 min. The beads were then filtered, left in open air for 30 min and were dried under diminished pressure at room temperature. Some of amidoximated samples were treated with NaOH solutions at 40°C (for example, for 24 h in 0.5 M NaOH), washed with distilled water until the washings became neutral and were dried under diminished pressure at room temperature prior to the sorption experiment.

Reagent grade products of AgNO₃, CdSO₄ · 8/3H₂O, CoCl₂ · 6H₂O, CuSO₄ · 5H₂O, NiCl₂, Pb(NO₃)₂, and Zn(NO₃)₂ · 6H₂O were used without further purification. In order to determine the uranium content, a sample of purchased UO₂(NO₃)₂ was converted to U₃O₈ by heating for 2 h at 900°C and weighed.

2.2 Sorption

The sorption experiments for Cu(II) were studied in an acetate buffer (pH 5.1) while aqueous solutions were used for other ions. The pH values for Ag(I), Cd(II), Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) solutions were 5.4, 5.3, 5.6, 4.3, 7.4, 4.4 and 5.4, respectively. A Cell-*g*-PAAmd sample (dry weight, 140 mg) and a metal salt solution (40 mM, 50 mL) were added to a flask and the content was shaken for a prescribed period (1–701 h) at 40°C. The amount of the metal sorbed by the sample was calculated from the decrease in the metal ion concentration of the solution. In the sorption experiments for UO₂(II), 20 mg of Cell-*g*-PAAmd sample and 100 mL of 0.42 mM UO₂(NO₃)₂ solution were used (experiments using uranium compounds in higher concentrations is not recommended in Japan).

The desorption of Cu(II) from Cell-*g*-PAAmd beads was studied in HCl and H₂SO₄ solutions. In a typical experiment, 430 mg of Cell-*g*-PAAmd sample which sorbed 56 mg of Cu(II) was added to a flask containing 100 mL of 0.7 M HCl and the mixture was kept at 15°C with shaking. The concentration of Cu(II) in the solution was measured at prescribed time intervals and the amount of Cu(II) desorbed was calculated.

2.3 Recycling

In a recycling experiment, the sorption–desorption cycle was repeated four times. A Cell-*g*-PAAmd sample treated with 0.5 M NaOH for 24 h at 40°C (510 mg) was

immersed in 40 mM CuSO₄ solution (50 mL), incubated for 24 h at 40°C and the amount of Cu(II) sorbed was determined (sorption). The beads were filtered off, washed with distilled water and dried with the procedure described in 2.1. Only a negligible amount of Cu(II), if any, was desorbed in the washing step. The washed beads were then soaked in 0.5 M H₂SO₄ (50 mL) for 1 h at 40°C and the amount of Cu(II) desorbed was determined (desorption). The beads were filtered off, washed with distilled water and dried with the aforementioned procedure. The dried beads were treated again with 0.5 M NaOH for 24 h at 40°C, washed and dried as before, and were used in the next cycle.

2.4 Analyses

Table 1 summarizes the quantitation methods for the metal ions. In the treatment of a sample solution containing uranium (0.5–10 mg) for analysis, 10 mL of 10% Na₂CO₃ and 3 mL of 10% NaOH were added to the solution and the volume of the solution was increased to 50 mL with water. The solution was then boiled until the volume was reduced to about 25 mL. After cooling, 5 mL of 10% NaOH and 3 mL of 3% H₂O₂ were added to the solution and the final volume was adjusted to 50 mL with distilled water for colorimetry.

The anion exchange capacity (AEC) and cation exchange capacity (CEC) of a Cell-*g*-PAAmd sample were determined from the amounts of HCl and NaOH consumed by the sample. A Cell-*g*-PAAmd sample (250 mg) was incubated in 0.1 M HCl (50 mL) for 24 h at 40°C. An aliquot (5 mL) was pipetted from the supernatant and titrated with 0.1 M NaOH. The apparent AEC value of the sample was calculated from

Table 1 Quantitation of Metal Ions

Ion	Salt	Quantitation	Indicator or Color Former
Ag(I)	AgNO ₃	Titration with NH ₄ SCN (0.05 M)	(NH ₄)Fe(SO ₄) ₂
Cd(II)	CdSO ₄	Titration with EDTA (0.01 M)	XO ^{a)}
Co(II)	CoCl ₂	Colorimetry (625 nm)	NH ₄ SCN
Cu(II)	CuSO ₄	Titration with EDTA (0.01 M) ^{b)}	PAN ^{c)}
Ni(II)	NiCl ₂	Colorimetry (465 nm)	dimethylglyoxime
Pb(II)	Pb(NO ₃) ₂	Titration with EDTA (0.01 M)	XO ^{a)}
UO ₂ (II)	UO ₂ (NO ₃) ₂	Colorimetry (580 nm)	H ₂ O ₂
Zn(II)	Zn(NO ₃) ₂	Titration with EDTA (0.01 M)	XO ^{a)}

^{a)}Xylenol Orange. ^{b)}In buffer at pH 5.1.

^{c)}1-(2-Pyridylazo)-2-naphthol.

the amount of HCl consumed. The beads were then washed with distilled water until the washings became neutral to Methyl Orange, then with acetone and dried under diminished pressure at room temperature. The dried sample (170 mg) was kept in 0.1 M NaOH (50 mL) for 24 h at room temperature with shaking. An aliquot from the supernatant (5 mL) was used for the determination of the amount of NaOH consumed (A). Another aliquot (5 mL) was used for the determination of the amount of the chloride ion liberated (B). The apparent CEC value was calculated from the difference, A-B.

3. Results and Discussion

3.1 Contents of Ionizable Groups

The amidoxime compounds are amphoteric and hence soluble in both acidic and alkaline solutions [3], and amidoxime groups coordinate to many kinds of metal ions. The amidoxime content of the bead cellulose having amidoximated polyacrylonitrile or polyacrylamidoxime grafts (Cell-g-PAAMD) was calculated from the nitrogen content of bead cellulose grafted with polyacrylonitrile (Cell-g-PAN) and that of Cell-g-PAAMD derived from it assuming that no side reaction had occurred [12]. In the Cell-g-PAAMD samples, however, functional groups other than amidoxime are considered to be present in addition to intact nitrile group, such as hydroxamic acid, carboxylic acid [13] and imidedioxime [14] groups. Most of these groups were also effective in the sorption of heavy metal ions [14-17] when introduced into resins.

The contents of ionizable groups were estimated with the apparent value of anion exchange capacity (AEC, or the amount of proton accepting groups) and with that of cation exchange capacity (CEC, or the amount of proton releasing groups) [18]. Fig. 1a shows AEC, CEC and the amount of Pb(II) sorbed (for 211 h at 40°C) as a function of the calculated amidoxime content. The three values increased with increasing amidoxime content with some extent of fluctuation. Fig. 1b shows that the amount of Pb(II) sorbed increased steadily with increasing AEC. The CEC showed a similar tendency but the linearity was much inferior. These findings show that the assumption adopted in the calculation of amidoxime content did not always hold and some side reactions must have occurred during amidoximation to

Fig. 1 Relation among AEC, CEC, amount of Pb(II) sorbed and amidoxime content. Sorption conditions; for 211 h at 40°C in 40 mM $\text{Pb}(\text{NO}_3)_2$ solution.

an extent different from sample to sample. For most Cell-g-PAAMD samples, the AEC value was higher than the CEC value and the difference became larger if the amount of NaOH consumed by the stem cellulose (0.907 mmol/g dry sample) was subtracted from the CEC value. This suggests that the conversion of amidoxime groups to hydroxamic acid and/or carboxylic acid groups did not occur to a large extent. Another possible reason is that the amidoxime group of Cell-g-PAAMD is relatively a base rather than an acid [19]. A Cell-g-PAAMD sample having next analytical values (Sample No. 1) was used in the following experiments unless otherwise noted: amidoxime content, 2.99 mmol/g dry beads; AEC, 4.51 meq/g dry beads; CEC, 3.74 meq/g dry beads.

3.2 Sorption Behavior

Table 2 summarizes results of the sorption of eight kinds of metal ions for 1 h at 40°C. Original Cell-g-PAAMD beads were yellow and the color clearly

changed to deep green and red after the sorption of Cu(II) and $\text{UO}_2(\text{II})$, respectively.

Fig. 2a shows the time courses of sorption of Ag(I), Cd(II), Cu(II), Pb(II), $\text{UO}_2(\text{II})$ and Zn(II) at 40°C by Cell-g-PAAmd beads without the NaOH treatment. The amount of ion sorbed from 40 mM solution in a fixed period and hence the sorption rate increased in the order $\text{Ni}(\text{II}) < \text{Cd}(\text{II}), \text{Co}(\text{II}), \text{Zn}(\text{II}) < \text{Pb}(\text{II}) < \text{Cu}(\text{II}) \ll \text{Ag}(\text{I})$. This order was the same as that observed for cellulose derivatives enriched in carboxyl groups [17]. For Pb(II), Cu(II) and Ag(I), the amounts sorbed at the longest sorption time examined were large but the ratios to AEC values were below 0.5. The value for Cu(II) was comparable to that reported for an amidoximated cellulose sample [5].

Table 2 Sorption of Metal Ions by Cell-g-PAAmd^{a)}

Ion	Without NaOH treatment		After NaOH treatment	
	mg/g ^{b)}	mol/mol ^{c)}	mg/g ^{b)}	mol/mol ^{c)}
Ag(I) ^{d)}	104.4	0.32	288.0	0.89
Cd(II)	2.0	0.006		
Co(II)	11.3	0.04		
Cu(II) ^{e)}	32.4	0.11	121.3	0.40
Ni(II) ^{e)}	0.0	0.0	21.1	0.07
Pb(II) ^{d)}	53.0	0.09	403.0	0.65
$\text{UO}_2(\text{II})$ ^{d)}	68.5	0.10	149.2	0.21
Zn(II)	8.1	0.04		

^{a)}Sorption; for 1 h at 40°C. The initial concentrations of metal ions were 40 mM except for $\text{UO}_2(\text{II})$ (0.42 mM). Cell-g-PAAmd sample No. 1 was used for Ag(I), Cd(II), Pb(II), $\text{UO}_2(\text{II})$ and Zn(II). The amidoxime content of the sample used for Co(II), Cu(II) and Ni(II) was 4.82 mmol/g dry beads. Its AEC and CEC values were not measured. ^{b)}metal mg/g dry beads. ^{c)}metal mol/mol amidoxime group. ^{d)}NaOH treatment; for 24 h at 40°C in 0.5 M NaOH. ^{e)}NaOH treatment; for 38 h at 40°C in 0.1 M NaOH.

At the initial stages, the mole number of Ag(I) sorbed per weight of beads was more than three times larger than that for $\text{UO}_2(\text{II})$ in a fixed sorption period (Table 2). However, the initial concentration of $\text{UO}_2(\text{II})$ was 0.42 mM which was about 1% of those of Ag(I) and other metal ions (40 mM). In a separate experiment, the amount of Ag(I) sorbed in 4 h increased almost linearly with increasing Ag(I) concentration up to 40 mM. This suggests that, at the same solution

Fig. 2 Time course of sorption at 40°C: (a) by Cell-g-PAAmd No. 1 without NaOH treatment; (b) beads were soaked in 0.1 M NaOH for 24 h at 40°C before the sorption experiments. Ion concentration; 0.42 mM for $\text{UO}_2(\text{II})$ and 40 mM for others.

concentration, the sorption rate for $\text{UO}_2(\text{II})$ at initial stages would be about thirty times higher than that for Ag(I).

3.3 NaOH Treatment

The alkali treatment of amidoxime resins accelerated the sorption of metal ions [20,21]. The treatment with NaOH solutions caused the swelling of Cell-g-PAAmd beads and the diameters became about three times larger than those before the treatment. After the sorption of Cu(II), the beads contracted to a size close to that before the NaOH treatment. Bead cellulose and Cell-g-PAN samples did not swell after the treatment in 0.1 M NaOH for 24 h at 40°C.

Fig. 2b shows the time dependence of sorption by NaOH-treated beads for Ag(I), Pb(II) and $\text{UO}_2(\text{II})$. Table 2 shows that the NaOH treatment increased remarkably the amount of metal ion sorbed and hence the sorption rate for Ag(I), Cu(II), Ni(II), Pb(II) and

$\text{UO}_2(\text{II})$. More than 60 % of the total sorption was achieved within 1 h. AEC and CEC values increased but only slightly after the NaOH treatment (for example, from 4.51 to 4.96 meq/g for AEC and from 3.74 to 3.76 meq/g for CEC). The increase in the sorption rate can be ascribed to the swelling while that in the amount of metal ion sorbed may be explained in terms of the increase in the amount of functional groups accessible to metal ions.

The treatment of Cell-*g*-PAAmd beads in 0.7 M HCl for 1 h at 40°C also accelerated the sorption of Cu(II) but it was less effective as compared with the NaOH treatment. The amounts of Cu(II) sorbed were larger by 40% and 4% at the sorption periods of 2 and 9 h, respectively, as compared with the case for untreated beads. After another acid treatment, in 0.5 M H_2SO_4 for 1 h at 40°C, Cell-*g*-PAAmd beads swelled only slightly (less than 10% in diameter). These findings show that the presence of negatively charged groups in Cell-*g*-PAAmd beads caused the swelling and the increase in the amount of metal ion sorbed. Each anionic group, such as amidoximate or carboxylate group, is considered to affect the sorption behavior of NaOH-treated samples in a different way. The amidoxime group was effective for the recovery of uranium from seawater while the carboxyl group was not [22]. It may be inferred that the amidoxime group was primarily effective for the sorption of metal ions and the carboxyl group was important for the swelling.

3.4 Recycling

For the recycling of sorbents which is important from practical view points, it is necessary to desorb effectively the metal ions sorbed. Fig. 3 shows the desorption of Cu(II) in 0.7 M HCl at 15°C. More than 80% of Cu(II) sorbed was desorbed in 15 min and the desorption leveled off at about 90% in 1 h. Almost all the Cu(II) sorbed will be desorbed under strongly acidic conditions but the decomposition of amidoxime and other moieties would occur simultaneously as in the case of other amidoxime resins [23]. Therefore, the desorption under highly acidic conditions was not studied.

Fig. 4 shows the change in the infrared spectrum for Cell-*g*-PAAmd beads during recycling. A band assignable to the amidoxime group was observed around 1660 cm^{-1} . An additional band appeared at

Fig. 3 Desorption of Cu(II): 430 mg of NaOH-treated Cell-*g*-PAAmd beads containing 56 mg of Cu(II) sorbed. NaOH treatment; for 62 h at 40 °C in 0.1 M NaOH.

about 1560 cm^{-1} after the NaOH treatment ascribable to carboxylate groups (Figs. 4b and 4d) and it shifted to 1700 cm^{-1} after the H_2SO_4 treatment (Figs. 4c and 4e, free carboxyl groups). The absorption at 1104 cm^{-1} observed in the latter figures was due to sulfate ion. The relative intensity of carboxyl bands seemed to increase slightly while that of amidoxime band decrease due to the repetition of recycling. These findings shows that carboxyl groups were present in an appreciable amount in addition to amidoxime groups in NaOH-treated Cell-*g*-PAAmd beads.

Four cycles of sorption–desorption experiments

Fig. 4 Change in infrared spectrum of Cell-*g*-PAAmd beads during recycling.

were carried out to examine the adaptability of Cell-*g*-PAAmd beads for recycling and results are shown in Fig. 5. In the case of samples without the NaOH treatment, the amount of Cu(II) sorbed at 40°C in 24 h decreased considerably with the repetition number. For these untreated samples, the sorption time of 24 h was much shorter than that necessary to reach the sorption equilibrium, and the decrease in the amount of Cu(II) sorbed can be ascribed to the decrease in the rate of sorption. One of the possible explanations is that Cu(II) ions remaining in the beads after the desorption might form crosslinking points to decrease the water content of the beads. As described in the above section, the sorption of Cu(II) caused the deswelling of NaOH-treated beads. For the sample which was treated with 0.5 M NaOH solution for 24 h at 40°C after each desorption process, the amount of Cu(II) sorbed also tended to decrease but the decrease was relatively small as compared with that for the beads without the NaOH treatment.

Cell-*g*-PAAmd beads studied here sorb several kinds of metal ions. However, their sorption performance seems not to be satisfactory for practical purposes although they have high relative surface area and sufficient mechanical strength. If appropriate improvement will be achieved in increasing amidoxime content and the degree of swelling, Cell-*g*-PAAmd beads will be useful for sorption of several kinds of

metal ions from aqueous solutions such as the recovery of uranium from seawater in which the uranium concentration is about 10^{-2} μ M.

Acknowledgment

The authors wish to thank Prof. Hiroshi Tomiyasu and Dr. Masayuki Harada, Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, for permitting to use the equipment necessary for the uranyl sorption experiments.

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Fig. 5 Repeated use of Cell-*g*-PAAmd beads. Sorption; for 24 h at 40°C in 40 mM CuSO₄ solution; Desorption; for 1 h at 40°C in 0.5 M H₂SO₄. Cell-*g*-PAAmd; No. 1.

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