

Binding of Heavy Metal Ions by Chemically Modified Woods*

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Synopsis

Three chemically modified woods were prepared and used for the binding of heavy metal ions. Wood-polyethylenimine composite (wood-PEI) was found to be effective for the adsorption of heavy metal ions such as Hg^{2+} , Cu^{2+} , and other metal ions which tend to form stable ammine complexes. Adsorption of metal ions on a wood-PEI derivative containing dithiocarbamate group (DTC-wood) was higher than that by wood-PEI. Especially, the reactivity of DTC-wood with Hg^{2+} was quite high and the binding capacity of about 5 mmol/g was easily attainable. The rate of adsorption on these wood-based adsorbents was very high, and adsorption of about 70% of total binding capacity was accomplished in the first 1 h. This may be due to a highly porous structure and a hydrophilic nature of the wood which constitutes the skeleton of the adsorbents. Amidoximated wood (AO-wood) prepared by the reaction of cyanoethylated wood with hydroxylamine showed selective adsorptivity for uranium in sea water. More than 53% of uranium in the sea water used was adsorbed by the AO-wood.

INTRODUCTION

The presence of toxic heavy metal ions in industrial and mining waste waters has become a serious problem from the viewpoint of environmental pollution. Further, in this period of restrictions on natural resources and energy, increasing efforts have been directed to recovering and utilizing useful materials, especially uranium in seawater. Although the uranium concentration in seawater is extremely low (3.3 parts per 10^9), the total amount is enormous (estimated to be $4\text{--}4.5 \times 10^9$ tons).

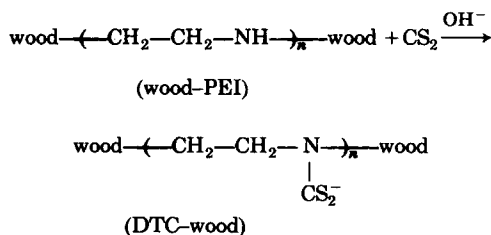
It is known that some methods can be used to remove heavy metal ions from solution. Utilization of chelating resins as substrates to recover heavy metal ions provides an effective means of solving waste water problems. Though some synthetic chelating resins have already been prepared and examined for waste water, those are rather impractical because of their high costs and their low adsorption capabilities, i.e., the velocity and the capacity of adsorption are generally low and small. Therefore, it is desired to prepare new chelating resins which are readily available for removing or concentrating toxic metals or useful metals.

It has also been reported that natural substances such as barks,¹⁻³ wool,⁴ chitin,⁵ and other agricultural byproducts⁶ are potentially useful for removal

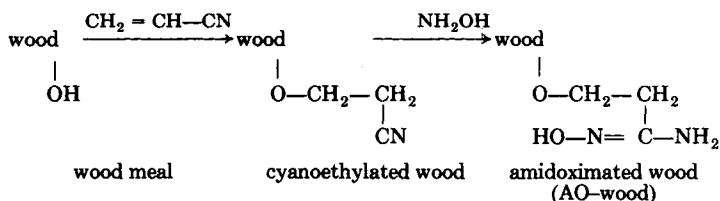
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of Hg^{2+} and other toxic metals. However, their binding capacities are relatively small.

Wood has a highly porous structure and a hydrophilic nature. Therefore, three chemically modified wood adsorbents as substrates for binding metal ions were examined. Polyethylenimine is known to be a good chelating agent for various metal ions. In the previous paper⁷ it was reported that ethylenimine was easily and efficiently polymerized in woody materials previously treated in a corona discharge. It is well known that secondary amines give dithiocarbamates through the reaction with carbon disulfide. Dithiocarbamates are effective chelating agents and have been used in an analytical chemistry.⁸ Hence, wood-polyethylenimine composite (wood-PEI) was further converted into dithiocarbamated wood (DTC-wood) by the reaction with carbon disulfide as shown below:



Amidoximes which are easily obtained by the reaction of hydroxylamine with compounds containing nitrile groups also form chelates with various metals.⁹ The amidoximation of wood is represented as follows:



In this paper, the chelating properties of the wood-PEI and the DTC-wood with several toxic metal ions and the adsorption of uranium from seawater on the AO-wood were examined. For comparison, two commercial resins, a dithizone type resin which is known to be highly selective for mercury and a selective adsorption resin for uranium, are also examined.

EXPERIMENTAL

Materials

Wood meal (42-80 mesh) of Akamatsu (*Pinus desiflora* SIEB. et ZUCC.), or Buna (*Fagus crenata* BL.) were used after extraction with alcohol-benzene (1:2). Ethylenimine was prepared by a modification of the procedure of Iwakura,¹⁰ which was similar to that proposed by Wenker.¹¹ Small quantities (100 mL) of the material were purified by distillation and the fraction collected in the range 55-57°C was employed in experiments. Mono-

ethanolamine, acrylonitrile, and other chemicals were reagent-grade commercial materials and used without further purification. Seawater containing 3.0 ppb of uranium ion was sampled at the Tsuyazaki seashore, Fukuoka Prefecture, Japan, and was filtered through a G-4 glass filter to remove suspended particles.

Preparation of Woody Adsorbents

Wood-PEI. Wood-PEI was readily prepared by a corona-induced polymerization method.⁷ A typical procedure was as follows: Wood meal (Akamatsu) was treated in a corona discharge (60 Hz) in air for 30 min, and then placed in an autoclave. Polymerization of ethylenimine onto the corona-treated wood meal was accomplished by the use of vapor phase reaction at 60°C for 5 h with stirring. The reaction product was washed with 1*N* acetic acid, water and methanol, and then dried *in vacuo*. PEI content of the product was determined by a Kjeldahl method. In this manner, several samples of differing PEI content were prepared.

DTC-Wood. DTC-wood was prepared by the treatment of the wood-PEI with carbon disulfide in the presence of sodium bicarbonate catalyst at 20°C for 1 h. The products were analyzed for nitrogen and sulfur content to determine the extent of the reaction according to Kjeldahl method for nitrogen and Schöniger's flask combustion method for sulfur.¹²

AO-Wood. AO-wood was prepared by the reaction of cyanoethylated wood with hydroxylamine in the following way:

Cyanoethylation of Wood. CE-wood was prepared by cyanoethylation of wood meal in the presence of alkaline salts, as described previously.¹³ Wood meal (Buna) was steeped for 30 min in a 4% sodium hydroxide solution approximately saturated with sodium thiocyanate (swelling agent). It was then squeezed out to a wet pickup of 150%. The wet wood meal was quickly placed into a kneader and allowed to react with a desired amount of acrylonitrile at 40°C for 4 h. After the reaction, a slight excess of acetic acid was added to neutralize the alkali catalyst. The product was well washed with water and then dried *in vacuo*.

Conversion of Cyanoethylated Wood into AO-Wood. AO-wood was prepared by the reaction of cyanoethylated wood with hydroxylamine in methanol at 67°C for 3 h. The reaction product was washed with water and methanol, and then air-dried at room temperature. The degree of conversion of CE group into AO group was calculated from the increments of nitrogen content of the reaction products.

Adsorption of Metal Ions

Metal ions, Hg^{2+} , UO_2^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , and Mg^{2+} were examined. Metal salts were dissolved in Clark-Lubs' buffer solution in order to keep the pH constant during the adsorption experiment. The adsorption measurement was made by equilibrating for a definite time at room temperature under mechanical shaking. The amount of the metal ion adsorbed on the sample was determined by the changes of the concentration of the metal ion in the solution. The metal ion concentration was determined by chelatometry. In the

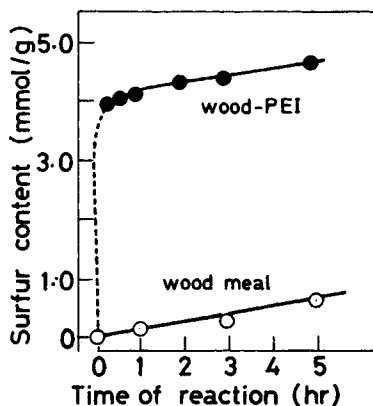


Fig. 1. Time course of reaction of wood-PEI with carbon disulfide at 20°C. Reaction condition: wood-PEI (PEI content = 24%) 1 g, CS₂ 34.7 mmol in 50 mL of 0.1N Na₂CO₃.

case when the concentration of remaining metal ion (Hg²⁺) was less than 100 ppm, a colorimetric method was used with the use of dithizone.¹⁴

Adsorption of Uranium from Seawater on AO-Wood

A batch equilibration technique was employed. The method involved equilibrating a weighed sample with 5 L of seawater under stirring for a definite time at room temperature. After the adsorption, the adsorbent was filtered off. The uranium was eluted from the adsorbent with 1M ammonium carbonate solution for 1 h at room temperature. The uranium concentration of the eluted solution was determined by a colorimetric method with the use of arsenazo III according to the method by Ohnishi and Hori.¹⁵

RESULTS AND DISCUSSION

Chemical Modification of Wood

Wood-PEI. Ethylenimine (EI) was remarkably polymerized onto the wood meal pretreated in a corona discharge, and the PEI of about 90% of total polymerized EI was fixed on the substrate.

DTC-Wood. The carbamation of the wood-PEI proceeded easily. Figure 1 shows the time course of the carbamation reaction at 20°C. At the first measurement point of 15 min the sulfur content of the sample had already reached to 4 mmol/g, and after this point the sulfur content increased gradually owing to the occurrence of the xanthation of hydroxyl groups in the wood with carbon disulfide. It is clear that the carbamation of the wood-PEI proceeds very fast. The DTC-wood which was used for the metal adsorption measurement contained sulfur of 4.34 mmol/g and nitrogen of 4.82 mmol/g. This indicates that approximately 45% of the imino groups was converted into dithiocarbamate groups. The obtained composites were stable on keeping under wet conditions below 10°C.

AO-Wood. The cyanoethylation of wood proceeded easily in the presence of alkaline salts. If wood meal was pretreated in a sodium hydroxide solution

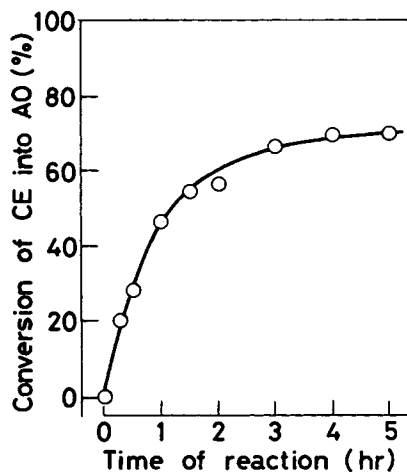


Fig. 2. Conversion of cyanoethylated wood into AO-wood at 67°C. Reaction condition: CE-wood (nitrogen content = 9.2%) 1 g, NH_2OH 37.5 mmol in 25 mL of methanol.

of high concentration (20%), the nitrogen content of the reaction product was low. This low value was probably due to the cleavage of the cyanoethyl/cellulose bonds by the strong alkali used. However, neutral swelling agent, sodium thiocyanate, in conjunction with dilute alkali increased accessibility of wood substrate and resulted in high nitrogen content of the CE-wood (nitrogen content = 9–10%). Further, more than 85% of the original wood meal was recovered.

Figure 2 shows the time course of the reaction of cyanoethylated wood with hydroxylamine. The conversion of cyanoethyl groups into amidoxime groups proceeded rapidly to about 60% within the first 2 h, and then gradually increased to about 70%.

Adsorption of Metal Ions on the Wood-PEI and the DTC-Wood

During the course of adsorption of metal ions on resins color changes were observed. The colors of the wood-PEI metal complexes are similar to those of ammine complexes. For example, Cu^{2+} complex was blue. The DTC-wood become dark brown with Cu^{2+} and some other metal ions. This color change of the DTC-wood shows that functional groups containing sulfur atoms were certainly introduced into the wood-PEI.

Adsorption Capacities. The effect of PEI content of the wood-PEI on the adsorption of heavy metal ions at pH 6 for 96 h is shown in Figure 3.

The wood-PEI was found to form quite stable chelates with heavy metal ions such as Hg^{2+} , UO^{2+} , Cu^{2+} , and Cd^{2+} . The adsorption capacities of these metal ions increased linearly with an increase in the PEI content of the wood-PEI. Thus, these indicate that the wood-PEI forms chelates with metal ions in constant ratios at any PEI content of the sample.

Table I shows the adsorption of various metal ions on the wood-PEI, the DTC-wood, and a commercial dithizone type resin at pH 6 for 23 h. The results in Table I showed the high capacity of the wood-PEI and the DTC-wood for binding metal ions except for Mg^{2+} . The order of the capacity

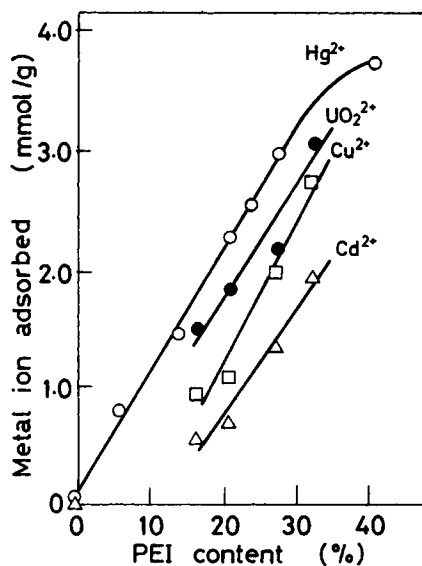


Fig. 3. Effect of PEI content of wood-PEI composites on the adsorption of Hg^{2+} , UO_2^{2+} , Cu^{2+} , and Cd^{2+} .

TABLE I
Metal-Ion Binding to the Wood-PEI, the DTC-Wood, and
a Commercial Dithizone Type Resin^a (mmol/g adsorbent)

Metal ion	Wood-PEI	DTC-wood	Commercial resin
Hg^{2+}	2.30	4.97	4.67
Cu^{2+}	1.10	1.82	1.18
UO_2^{2+}	1.85	1.24	0.46
Zn^{2+}	0.92	1.19	0.11
Cd^{2+}	0.65	0.98	—
Ni^{2+}	0.95	0.71	0.11
Mg^{2+}	0.20	0.05	0.19

^aMetal ion concentration = 0.01 mol/L.

of adsorption was $\text{Hg}^{2+} > \text{UO}_2^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Mg}^{2+}$ for the wood-PEI. In the case of the DTC-wood, the order was $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{UO}_2^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+} \approx 0$. These orders were almost in agreement with the stability constants for ammine complexes, such as ethylenediamine-metal complexes¹⁶ and dithiocarbamate complexes.⁸ Comparison of the binding by the DTC-wood with that by the wood-PEI reveals binding capacity-increment of 2.67, 0.72, 0.33, and 0.27 mmol/g adsorbent for Hg^{2+} , Cu^{2+} , Cd^{2+} , and Zn^{2+} , respectively. The binding of Hg^{2+} by the DTC-wood which contains sulfur and nitrogen atoms was twice higher than that by the wood-PEI containing only nitrogen atoms, and was comparable to that by the commercial dithizone type resin, the selective adsorption resin for mercury. It is clear that the DTC-wood is quite effective for the adsorption of mercury.

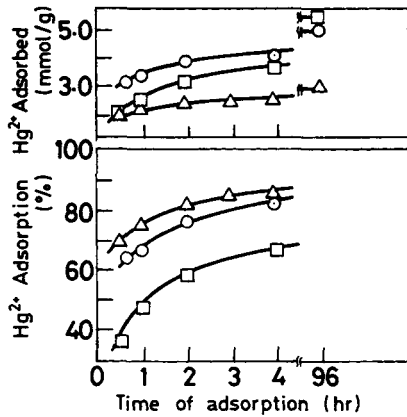


Fig. 4. Initial adsorption rate of Hg^{2+} of pH 6 on wood-PEI (Δ), DTC-wood (\circ), and a commercial dithizone type resin (\square).

Rate of Adsorption. Figure 4 shows the rate of adsorption for Hg^{2+} . In the case of the wood-PEI and the DTC-wood, adsorption of about 70% of the total binding capacity was accomplished in the first 1 h; then the amount of adsorption increased gradually and reached equilibrium in 96 h. It can be seen that initial rate of adsorption on wood-based adsorbents are higher than that on the commercial resin. This may be due to a highly porous structure and a hydrophilic nature of wood substrate which constitutes the skeleton of the adsorbents. The higher initial rate of adsorption on wood-based adsorbents is obviously effective for practical use for binding metal ions from waste water, especially when column flow operation is desired.

Effect of pH. Figure 5 shows the effect of pH on the adsorption of several metal ions on the DTC-wood and the commercial dithizone type resin. In the case of the DTC-wood, the amount of Zn^{2+} , Cd^{2+} , and Ni^{2+} adsorbed varied with pH, while the adsorption of Hg^{2+} and Cu^{2+} showed no pH dependence

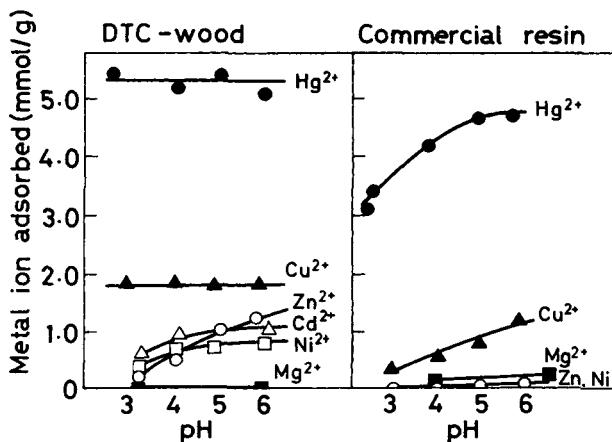


Fig. 5. Effect of pH on the adsorption of Hg^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , and Mg^{2+} on DTC-wood and a commercial dithizone type resin.

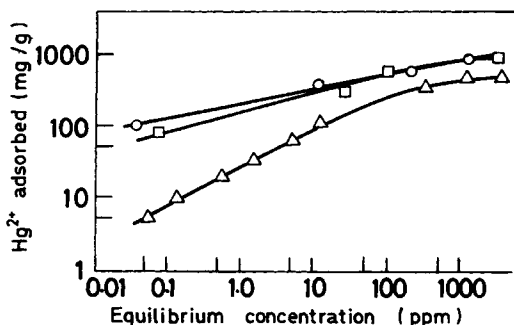


Fig. 6. Adsorption isotherms for binding of Hg^{2+} to wood-PEI (Δ), DTC-wood (\circ), and a commercial dithizone type resin (\square).

within the pH range examined. Therefore, separation of Hg^{2+} or Cu^{2+} from other metal ions can easily be carried out by varying the pH.

Influence of Hg^{2+} Concentration. The adsorption isotherms for binding of Hg^{2+} on the wood-PEI, the DTC-wood, and the commercial dithizone type resin were determined in order to find out the extent of the adsorption of Hg^{2+} from dilute solution. The results are shown in Figure 6. The wood-PEI adsorbed a considerable amount of Hg^{2+} at higher concentrations of the solution. The DTC-wood exhibited the highest adsorbability among the three adsorbents. Especially, at low concentration (below 0.1 ppm Hg), the DTC-wood showed more than 20 times as high adsorptivity as that of the wood-PEI. The DTC-wood can easily lower the concentration of Hg^{2+} below 0.05 ppm.

Another characteristic of these wood-based adsorbents is that the adsorption of Hg^{2+} is barely affected by the presence of anions such as Cl^- , NO_3^- , and SO_4^{2-} with the concentration range examined as shown in Table II.

Adsorption of Uranium from Seawater on the AO-Wood

Many kinds of procedures to extract uranium from seawater have so far been studied, and hydrous titanium oxide has been evaluated to be the most excellent adsorbent for uranium in sea water.¹⁷ Recently, it was reported that

TABLE II
Effect of the Coexistence of Anions on the Adsorption of Hg^{2+}
on Wood-PEI and DTC-Wood^a

Anion species	Concentration of anion (M)	Wood-PEI (mmol/g)	DTC-wood (mmol/g)
NO_3^-	0	2.79	4.53
	0.5	2.79	4.50
	1.0	2.76	4.49
Cl^-	0.5	2.77	4.53
	1.0	2.77	4.51
SO_4^{2-}	0.5	2.79	4.50
	1.0	2.80	4.48

^a Hg^{2+} concentration = 0.01 mmol/L.

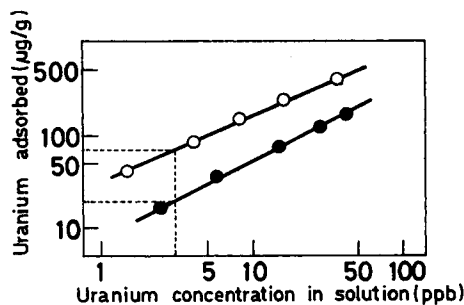


Fig. 7. Adsorption isotherms for binding of uranium ion to AO-wood (\circ , AO group = 3.9 mmol/g) and a commercial selective resin for uranium (\bullet).

the extraction of uranium by chelating resins^{18,19} or fibers²⁰ containing amidoxime groups was more effective than that by inorganic adsorbents such as hydrous titanium oxide.

Amidoximes are easily obtained by the reaction of hydroxylamine with the compounds containing nitrile groups as shown before. Hence, the AO-wood was prepared by the reaction of hydroxylamine with cyanoethylated wood, and examined for the adsorption of uranium in seawater.

Adsorption Equilibrium. An example of adsorption equilibrium of uranium in seawater on the AO-wood containing the amidoxime group of 3.87 mmol/g is shown in Figure 7. The AO-wood, 0.2 g, was equilibrated with 5 L of seawater for 70 h. If necessary, seawater was enriched with uranyl acetate at the desired concentrations. The results followed Freundlich's isotherm as shown in Figure 7. The adsorption of uranium on the AO-wood is higher than that on a commercial selective resin for uranium. At the concentration of uranium in seawater (3 ppb) the binding of uranium by the AO-wood amounted to 3.6 times as large as that by the commercial resin, and 53% of uranium in seawater was recovered by the AO-wood, while only 21% was recovered by the commercial resin.

Adsorption Rate. Figure 8 shows the rate of adsorption for uranium in seawater on the AO-wood containing the amidoxime group of 3.27 mmol/g.

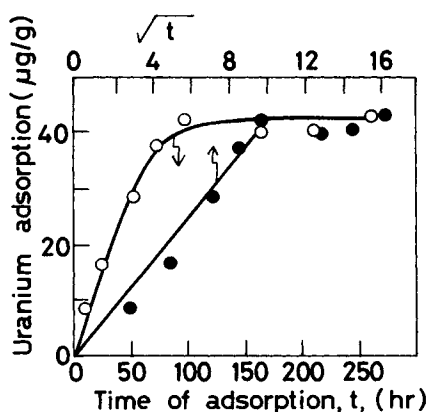


Fig. 8. Time course of adsorption of uranium in seawater on AO-wood. AO-wood (AO group = 3.2 mmol/g) 0.2 g, sea water 5 L.

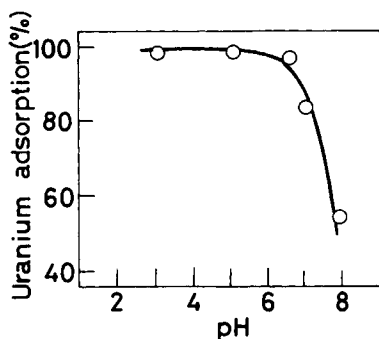


Fig. 9. Effect of pH on the adsorption of uranium from enriched seawater (1 ppm uranium) on the AO-wood (AO group = 3.0 mmol/g).

The amount of adsorption of uranium on the AO-wood increased with time of adsorption and reached equilibrium in 100 h. The binding of the uranium was approximately proportional to the square root of the time of adsorption. This indicates that the rate of diffusion of uranium ions into adsorbent is the rate-determining step in the adsorption of uranium.

Effect of pH. Effect of pH on the adsorption of uranium from seawater which was enriched to 1 ppm uranium concentration on the AO-wood for 25 h is shown in Figure 9. The adsorption of uranium on the AO-wood depended on pH. Fifty-three percent of uranium in the solution was adsorbed by the AO-wood at the pH 7.92, corresponding to the pH of natural seawater, but the amount of the adsorbed uranium increased steeply with the lowering in pH and 97% of uranium adsorbed by the AO-wood at pH 3-6.6 range.

CONCLUSIONS

Three chemically modified woods were prepared and examined for their applicability of concentrating trace metals from aqueous media. The following conclusions are obtained:

1. Wood-PEI is readily prepared by a corona-induced polymerization of ethylenimine onto wood-meal.
2. Wood-PEI is easily converted into DTC-wood by the reaction with carbon disulfide.
3. AO-wood is easily obtained by the reaction of cyanoethylated wood with hydroxylamine.
4. Rates of the adsorption of metal ions by these adsorbents are very high.
5. DTC-wood is quite effective for the adsorption of mercury.
6. AO-wood shows the selective adsorption ability for uranium in seawater.

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