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Kinetic Behavior of Lightly Crosslinked Chelating Resins Containing Amidoxime Groups for Batchwise Adsorption of UO_2^{2+}

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ABSTRACT

Lightly crosslinked poly(acrylonitrile-*co*-divinylbenzene) beads (RN-5) have been synthesized by suspension polymerization. The use of dichloroethane and chloroform as a porogen produced lightly crosslinked copolymer beads having highly porous structures. The chelating resins containing amidoxime groups (RNH-5) have been prepared by the reaction of copolymer beads with NH_2OH in MeOH. The resulting chelating resins have been used in the batchwise adsorption of UO_2^{2+} from nitrate solutions containing 0.01 $mol \cdot dm^{-3}$ UO_2^{2+} at pH 3.25. In order to get some measure of the relative performance of each resin in kinetic terms, the extraction of UO_2^{2+} was monitored with time and some adsorption profiles were obtained. An increase in porogen content resulted in a marked increase in the batchwise adsorption of UO_2^{2+}. Alkaline treatment allowed a high swelling and hence rapid accessibility of UO_2^{2+} to the ligands. Even after 30 minutes, the alkali-treated resins were 50% loaded.

INTRODUCTION

In recent years a wide range of chelating resins containing amidoxime groups has been developed and evaluated for their ability to recover

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uranium from seawater (1–15). Important properties of these resins include high capacity, high selectivity, and fast kinetics.

The modification of polymer networks by a porogenic agent has long been known to produce significant changes in their properties (16–20). We recently showed that the use of solvating diluents such as dichloroethane, tetrachloroethane, and chloroform during the synthesis of poly(acrylonitrile-*co*-divinylbenzene) resulted in copolymer beads having highly porous structures (21, 22). The resulting chelating resins containing amidoxime groups exhibited a marked adsorption rate for uranium in seawater. Furthermore, it was concluded that these chelating resins exhibit an overall improved performance than hitherto developed. Large-scale adsorption tests showed that the adsorption rates of these high-performance chelating resins were higher than those of the less porous analogues.

The resins used in this work were developed with the above factors in mind. The syntheses and analytical data have already been reported (21). This paper will describe the details of the batchwise adsorption tests for UO_2^{2+}.

EXPERIMENTAL

The copolymer beads of acrylonitrile and divinylbenzene (RN-5) were synthesized as previously described (5). All the resins prepared in the presence of dichloroethane and chloroform were 5 mol% crosslinked. The chelating resins (RNH-5) were prepared by the reaction of poly(acrylonitrile-*co*-divinylbenzene) beads with 3% hydroxylamine in methanol at 80°C for 2 hours. The ion-exchange capacities of the resins were determined by the usual methods (5). The pore volume and pore radius were obtained by using a Carlo-Erba mercury porosimeter (Model 1520). The specific surface area was measured on a Yuasa surface area apparatus, following the BET method.

Batch UO_2^{2+}-uptake experiments were performed using uranyl nitrate solution of 0.01 $mol{\cdot}dm^{-3}$ prepared from analytical grade $UO_2(NO_3)_2{\cdot}6H_2O$. Resin (50 mg) was contacted with a solution (20 cm^3) containing UO_2^{2+} (0.01 $mol{\cdot}dm^{-3}$) at 30°C with occasional shaking. The amount of UO_2^{2+} adsorbed (i.e., mmol UO_2^{2+}/g of resin) was calculated from the difference of the UO_2^{2+} concentration in the substrate before and after adsorption by the resin. For UO_2^{2+}, a simple and sensitive spectrophotometric method based on colored complexes with sodium salicylate in aqueous medium was calibrated using uranium standards. Into a 50-cm^3 volumetric flask was placed a measured volume of UO_2^{2+} solution containing UO_2^{2+} in the 8.4×10^{-3} to 21.0×10^{-3} mmol range followed by 1.0 cm^3 sodium salicylate (10%) and water to make up to the mark. The absorbance of the solution was measured at 468 nm wavelength.

The alkaline treatment was performed by using a 1.0 mol·dm^{-3} NaOH solution at 30°C for 72 hours.

RESULTS AND DISCUSSION

Properties of Chelating Resins

The data in Table 1 give the properties of resins prepared by varying the proportion of dichloroethane and chloroform as a porogenic agent from 60 to 120 vol% at a constant divinylbenzene content (5 mol%) during suspension polymerization. An increase in porogen content resulted in highly porous structures. The details of these resins and their structures have been reported before (21).

Bearing in mind that there is a relationship between porosity and the performance of a resin, the effect of changing the proportion of porogenic agent on the UO_2^{2+} adsorption was examined in batchwise adsorption experiments. The data in Table 2 show that increasing the content of dichloroethane and chloroform from 60 to 100 vol% resulted in a marked

TABLE 1
The Properties of Chelating Resins[a]

Porogen[b]		SSA (m^2/g)[c]		Pore volume (cm^3/g)	Average pore radius (Å)	C_a[d] (meq/g)	C_c[e] (meq/g)	V (NaCl)	
Name	Vol%	RN-5	RNH-5					(cm^3/g) (NT)[f]	(cm^3/g) (AT)[g]
DCE	60	40.9	21.5	0.335	225	3.7	1.2	2.0	3.2
DCE	80	49.4	25.7	0.345	229	3.8	1.5	2.2	3.6
DCE	100	71.6	30.8	0.435	256	3.8	1.6	2.6	4.1
DCE	120	67.3	31.4	0.393	202	3.8	1.6	2.6	4.7
CH	60	42.6	22.5	0.369	238	3.7	1.2	2.2	3.2
CH	80	44.6	24.2	0.362	240	3.7	1.5	2.4	3.6
CH	100	61.4	27.6	0.333	220	3.7	1.6	2.6	4.1
CH	120	72.7	29.7	0.304	168	3.8	1.6	2.7	4.6

[a] NH_2OH/CN (mol ratio): 1.5 during functionalization.
[b] DCE: Dichloroethane. CH: Chloroform.
[c] Specific surface area.
[d] Anion-exchange capacity.
[e] Cation-exchange capacity.
[f] Nontreated resin.
[g] Alkali-treated resin.

TABLE 2
Adsorption of UO_2^{2+} from 0.01 mol·dm^{-3} $UO_2(NO_3)_2$ Solution at pH 3.25 and 30°C

Resin	$[UO_2^{2+}]$ adsorbed[a] (mmol/g-resin)	$t_{1/2}$[b] (min)	Particle size (mesh size)
RNH-5(DCE-60)NT	0.656	54	32–60
RNH-5(DCE-80)NT	0.737	57	"
RNH-5(DCE-100)NT	0.797	60	"
RNH-5(DCE-120)NT	0.858	119	"
RNH-5(CH-60)NT	0.696	75	"
RNH-5(CH-80)NT	0.892	90	"
RNH-5(CH-100)NT	0.914	60	"
RNH-5(CH-120)NT	0.944	111	"
RNH-5(CH-120)AT[c]	1.142	33	"

[a] Adsorption time: 24 hours.
[b] Time to achieve adsorption to half the final capacity obtained after 24 hours.
[c] Alkali-treated resin.

increase in UO_2^{2+} adsorption, although all the resins are capable of adsorbing UO_2^{2+}. The increased adsorption abilities can be attributed to the highly porous structures of the resultant resins. The amount of UO_2^{2+} adsorbed was obtained after a 24-hour period for each resin. The maximum value of UO_2^{2+} adsorption for RNH-5(DCE) prepared at 120 vol% dichloroethane is 0.858 mmol UO_2^{2+}/g resin. The respective value for RNH-5(CH) prepared at 120 vol% chloroform is 0.944 mmol UO_2^{2+}/g resin.

Kinetic Behavior of Chelating Resins

In order to compare the relative performances of each resin in kinetic terms, the adsorption of UO_2^{2+} was monitored with time, with samples being taken at 15 and 30 minutes and at 1, 4, 8, and 24 hours. The adsorption profiles for RNH-5(DCE) and RNH-5(CH) are shown in Figs. 1 and 2, respectively. To provide some numerical basis for comparison of the resins, the time to achieve loading to half the final capacity (24 hours), $t_{1/2}$, was calculated from the profiles. The data are summarized in Table 2. Since the resin particle diameters were of similar magnitude, $t_{1/2}$ values are expected to represent a reasonable basis to compare the kinetic performances. The results show that resins with 60–80 vol% porogen content give a faster exchange with lower capacity. What is clear, however, is that resins prepared by using 100–120 vol% porogen achieve full UO_2^{2+} loading with a higher capacity. The $t_{1/2}$ values were only taken as a guide to the likely behavior of resins. Each resin has a broad particle size distri-

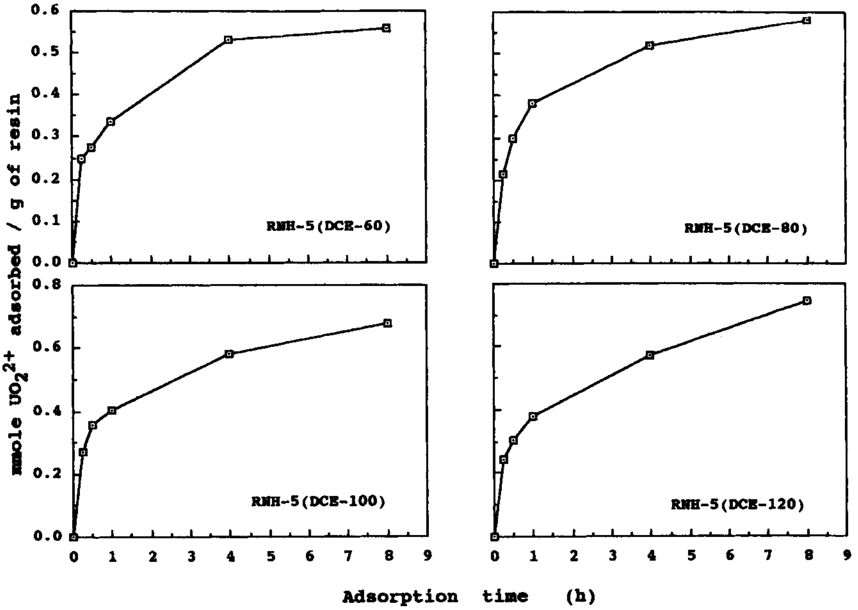

FIG. 1 Loading of chelating resins RNH-5(DCE) using 0.01 mol·dm^{-3} UO_2^{2+} at pH 3.25 and 30°C as a function of time.

bution, although the distributions are very similar. Therefore, no attempt will be made to give any conclusions about the adsorption mechanism from $t_{1/2}$ values alone.

Subsequent kinetic experiments confirmed the efficiency of adsorption of UO_2^{2+} by resin RNH-5(CH-120), and so the adsorption isotherm for UO_2^{2+} was produced for this resin by using UO_2^{2+} nitrate solutions with concentrations of 0.0025, 0.005, 0.01, and 0.02 mol·dm^{-3}. The isotherm barely reached saturation, even with a solution of 0.02 mol·dm^{-3} UO_2^{2+} nitrate. The isotherm is shown in Fig. 3.

Effect of Alkaline Treatment

The enhancement of the adsorption ability for uranium by the alkaline treatment has been reported before (9, 10, 21). The increased adsorption ability of the resulting resins was attributed to changes in the physical and chemical structures of the resins in alkaline medium.

As shown in Fig. 4, pretreatment of resins with 1.0 mol·dm^{-3} NaOH rendered them essentially active. The alkali-treated resins achieve high

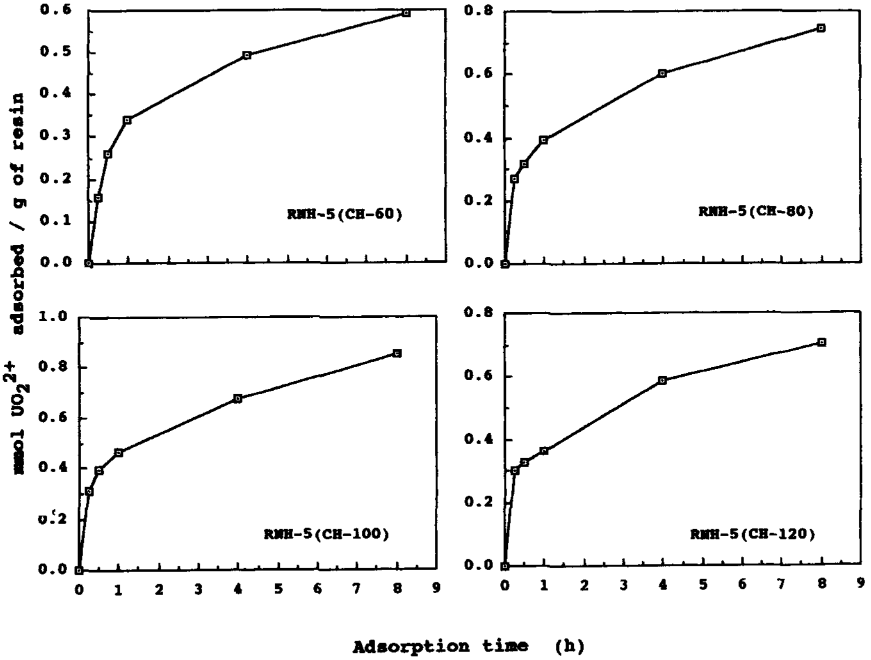

FIG. 2 Loading of chelating resins RNH-5(CH) using 0.01 mol·dm^{-3} UO_2^{2+} at pH 3.25 and 30°C as a function of time.

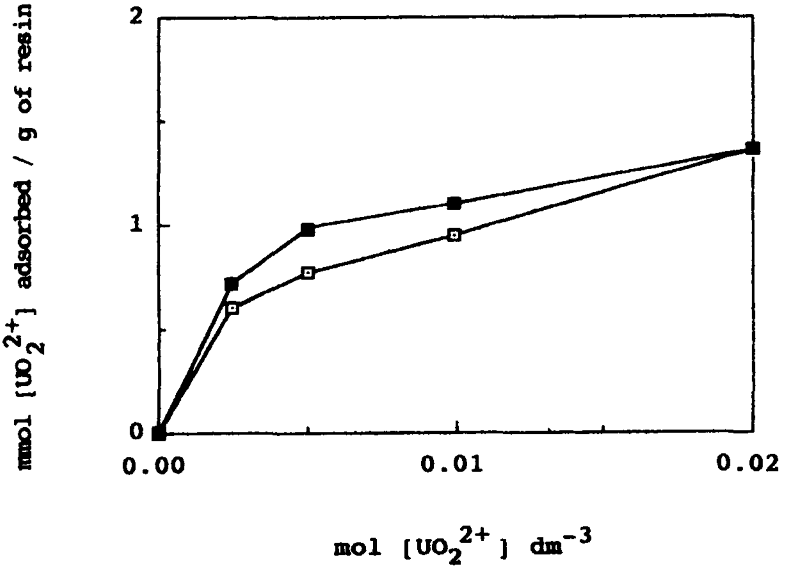

FIG. 3 UO_2^{2+} loading concentration isotherms, pH 3.25, 30°C, 24 hours. Resin, RNH-5(CH-120): (□) nontreated resin; (■) alkali-treated resin.

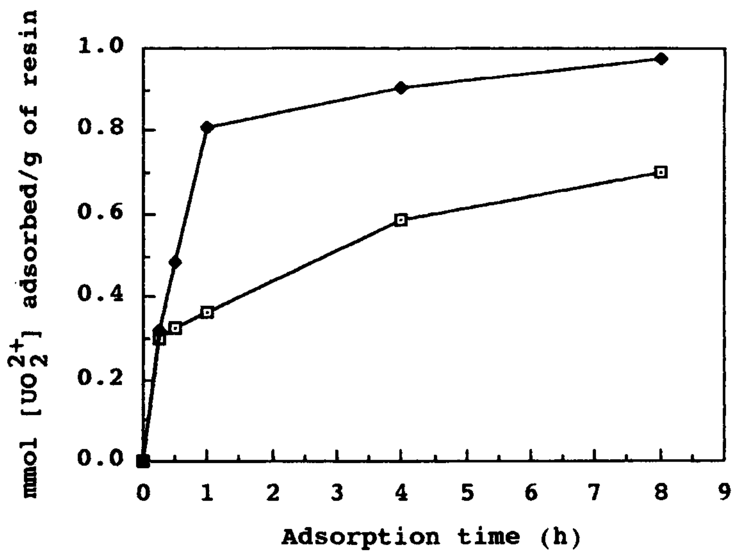

FIG. 4 Effect of alkaline treatment on UO_2^{2+} loading of chelating resins RNH-5(CH-120) using 0.01 mol·dm^{-3} UO_2^{2+} at pH 3.25 and 30°C as a function of time: (□) nontreated resin; (◆) alkali-treated resin.

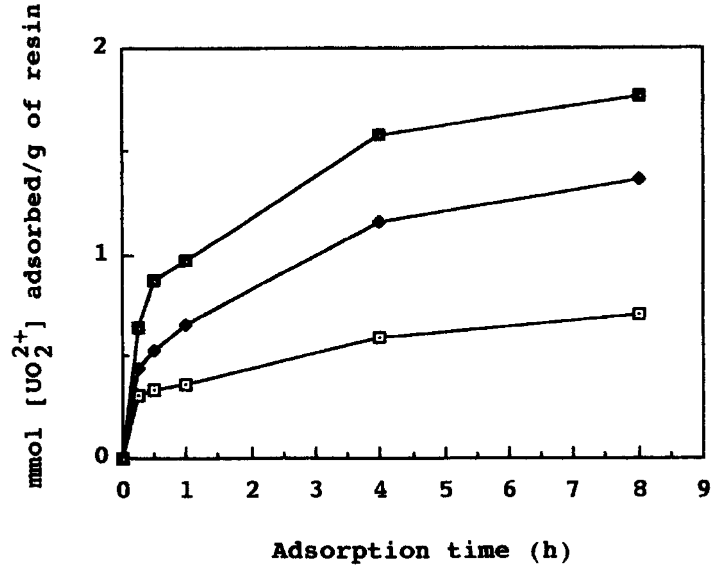

FIG. 5 Effect of temperature on the rate of loading of uranyl ions onto RNH-5(CH-120)NT at pH 3.25: (□) 30°C; (◆) 50°C; (■) 70°C.

UO_2^{2+} loading significantly more quickly than the nontreated ones. Even after 4 hours the alkali-treated resins were 79% loaded while the nontreated resins were 62% loaded. As illustrated in Fig. 3, the adsorption isotherm of the alkali-treated resin hardly reached saturation, even with a solution of 0.2 mol·dm^{-3} UO_2^{2+} nitrate. It is clear, however, that the alkali-treated resins reach saturation more quickly than do the nontreated ones.

Effect of Temperature

The adsorption of UO_2^{2+} with time was studied at 30, 50, and 70°C by using the standard batch adsorption procedure with 0.01 mol·dm^{-3} $UO_2(NO_3)_2$. The results are shown in Fig. 5. Temperature-dependent studies using resin RNH-5(CH-120) showed a significant increase in adsorption capacities at elevated temperatures. This implies that the chemistry of the complex formation itself might predominate in the ultimate control of the adsorption mechanism for UO_2^{2+}, rather than a diffusion mechanism.

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