Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Konishi, Yasuhiro , Asai, Satoru , Midoh, Yuji and Oku, Muneharu(1993) 'Recovery of Zinc, Cadmium, and Lanthanum by Biopolymer Gel Particles of Alginic Acid', Separation Science and Technology, 28: 9, 1691 — 1702
To link to this Article: DOI: 10.1080/01496399308019036
URL: http://dx.doi.org/10.1080/01496399308019036

SEPARATION SCIENCE AND TECHNOLOGY, **28**(9), pp. 1691–1702, 1993

Recovery of Zinc, Cadmium, and Lanthanum by Biopolymer Gel Particles of Alginic Acid

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ABSTRACT

Biopolymer gel particles of alginic acid were found to be a useful material for recovering zinc, cadmium, and lanthanum from aqueous solutions. The metals sorbed by the gel particles could be completely eluted by using dilute HCl solution of 0.1 kmol/m^3. The distribution ratios of the individual metals between the gel and liquid phases were measured by using a batch method. The equilibrium data were consistent with predictions made assuming that sorption takes place with the ion-exchange reaction between metal ions and alginic acid. The maximum sorption capacity of the gel particles and the distribution equilibrium constants for the metals were determined by comparing the experimental data with the theoretical predictions. The observed effect of temperature on the distribution equilibrium was insignificant in the range from 15 to 35°C.

INTRODUCTION

Synthetic polymers such as ion-exchange resins and chelating resins have been widely used as commercial sorbents to collect toxic metals, precious metals, base metals, and radionuclides from aqueous solutions. Many recent studies have addressed the recovery of heavy metal ions by naturally occurring polymers derived from biomass (1–7). Such biopolymers are likely to be potentially useful as new biosorbent materials for collecting various metal ions because of their low production costs and their excellent selectivity for multivalent metal ions.

This paper considers the use of alginic acid gel particles as a natural cation-exchange polymer for the recovery of metal ions. Alginic acid is

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a biopolymer carrying carboxyl groups capable of forming complexes with metal ions and occurs in brown seaweeds. The ability of alginate to form gels by ion-exchange reaction with multivalent metal ions suggests its use as a metal sorbent. There are several reports of the ion-exchange properties of alginates. Cozzi et al. (8) reported that the affinity of alginic acid for homologous ions of the periodic table can be correlated with the size of the hydrated ionic radius and decreases in the following order: Ba > Sr > Ca > Mg; Cd > Zn. Muzzarelli (1) observed that alginic acid has a high sorption capacity for transition metal ions compared with carboxylmethylcellulose. Kuyucak and Volesky (9) investigated the sorption mechanism of cobalt by using the nonliving algal biomass of *Ascophyllum nodosum* and found that alginates (carboxyl groups) of the cell wall play an important role in the sorption of cobalt from aqueous solution. Jang et al. (10) carried out experiments concerning the sorption equilibrium of copper by calcium alginate gel and used a modified Langmuir model to correlate the experimental data. Alginate gels were also used to recover cobalt and copper from an acidic cobalt ore leachate in a loop fluidized bed reactor (11). However, a limited amount of information is available concerning the sorption stoichiometry, the distribution equilibrium constants, and the maximum sorption capacity of alginate gels.

The objective of this work was to derive quantitative information on the sorption equilibria of zinc, cadmium, and lanthanum from aqueous solutions by gel particles of alginic acid. The distribution ratios of these metals between the gel and liquid phases were measured in a batch vessel. The equilibrium data were then analyzed to determine the maximum sorption capacity of gel particles and the distribution equilibrium constants.

EXPERIMENTAL SECTION

Materials

The alginic acid used in this study was prepared by the gelation of sodium alginate in aqueous HCl solution. The sodium alginate was produced from the common brown algae *Lessonia nigrescans* by Kibun Food Co., Japan. Figure 1 shows the apparatus used for preparing the gel particles of alginic acid. A viscous solution of 2.5 wt% sodium alginate was sucked through stainless steel pipes of 1 mm hole diameter by using a aspirator, and it was then added dropwise to a 1.0 kmol/m^3 HCl solution at room temperature. Gel particles of about 1.5 mm diameter were formed by the gelation due to a sodium ion–hydrogen ion exchange reaction. The gel particles were separated from the solution and washed with distilled water. Thorough washing was required to remove the HCl that had pene-

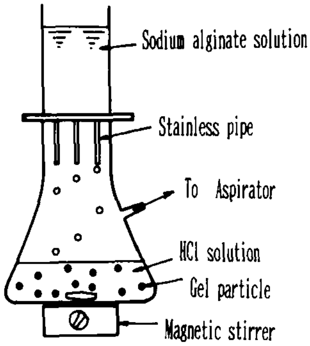

FIG. 1 Schematic representation of the apparatus for preparing gel particles of alginic acid.

trated into the gel phase. After that, the particles were dried at room temperature.

The test solutions used were aqueous solutions of $ZnCl_2$, $CdCl_2$, and $LaCl_3$, and their initial concentrations ranged from 5.0×10^{-4} to 2.5×10^{-2} kmol/m^3. The pH of the solutions was adjusted by adding NaOH or HCl. The ionic strength of the metal solutions was less than 7.5×10^{-2} kmol/m^3.

Experimental Procedure

Experiments were carried out by a batchwise method and most of the data were taken at 25°C. A mixture of the alginic acid gel particles and the metal solution was shaken for 2 hours or more in a flask with a stopper. The dry gel particles–solution loading ratio was 1.0 to 7.0 kg/m^3. After sorption equilibrium was reached, the mixture was filtered and the filtrate was saved for analysis. In some runs the solution samples to be analyzed were periodically withdrawn from the flask in order to investigate the sorption behavior as a function of time. The solution samples were analyzed for zinc and cadmium by atomic absorption spectrophotometry and for lanthanum by EDTA titration. The equilibrium pH of the solution was measured by using a pH meter. The concentration of metal in the gel phase was determined from the liquid phase mass balance. The distribution ratio of metal between the gel and liquid phases was calculated from the gel-phase concentration (number of moles per unit mass of dry gel) divided by the liquid-phase concentration (the number of moles per unit volume of solution).

DISTRIBUTION EQUILIBRIUM OF METAL

When the gel particles of alginic acid acts as a cation exchanger, the multivalent metal ions M^{n+} in the liquid phase exchange with the H^+ ions in the gel phase. The ion-exchange reaction is likely to be expressed as follows:

$$M^{n+} + n\overline{HR} \Leftrightarrow \overline{MR_n} + nH^+ \quad (1)$$

where overscoring indicates that a species is present in the gel phase, and HR denotes the acid-type functional groups (carboxyl groups). The equilibrium constant K_M for Reaction (1) is:

$$K_M = \overline{[MR_n]}[H^+]^n/[M^{n+}]\overline{[HR]}^n \quad (2)$$

where square brackets indicate species concentrations. The distribution ratio D_M of the metal between the gel and liquid phases is defined as

$$D_M = \overline{C_M}/C_M \quad (3)$$

where $\overline{C_M}$ is the total metal concentration in the gel phase and C_M is the total metal concentration in the liquid phase. When MR_n and M^{n+} are the only species containing the metal in the gel and liquid phases, the combination of Eq. (2) with Eq. (3) gives

$$D_M = K_M\overline{[HR]}^n/[H^+]^n \quad (4)$$

If equilibrium data are consistent with the above-mentioned theoretical approach, a log-log plot of D_M versus $\overline{[HR]}/[H^+]$ will yield a straight line with a slope of 3.0. In such cases the distribution equilibrium constant K_M can be evaluated from the intercept of the line. Clearly, a high pH and free functional group concentration $\overline{[HR]}$ will tend to promote the sorption of metal ions. On the other hand, a low pH will tend toward desorption of the metal from the gel phase.

Since the functional groups in the gel phase are consumed for binding the metal ions, the equilibrium concentration $\overline{[HR]}$ of free functional groups can be written in terms of the mass balance:

$$\overline{[HR]} = Q_{HR} - n\overline{[MR_n]} \quad (5)$$

where Q_{HR} is the initial concentration of functional groups in the gel phase, i.e., the maximum sorption capacity. Combining Eq. (4) and Eq. (5) gives

$$D_M = K_M(Q_{HR} - n\overline{[MR_n]})^n/[H^+]^n \quad (6)$$

The unknown constant Q_{HR} can be determined graphically by rearrangement of Eq. (6) into the following form:

$$\overline{[MR_n]} = -(1/n)(1/K_M)^{1/n}D_M^{1/n}[H^+] + (1/n)Q_{HR} \quad (7)$$

If a given set of experimental data is of the same mathematical form as Eq. (7), a plot of $\overline{[\mathrm{MR}_n]}$ versus $D_M^{1/n}[\mathrm{H}^+]$ should be linear with an intercept at $(1/n)Q_{\mathrm{HR}}$ and a slope of $-(1/n)(1/K_M)^{1/n}$.

RESULTS AND DISCUSSION

Sorption and Desorption Behavior

Several preliminary experiments were conducted to confirm the ability of alginic acid gels to recover lanthanum, zinc, and cadmium from aqueous solutions. The observed data are discussed below.

Figure 2 shows the sorption and desorption behavior of lanthanum by gel particles as a function of time. The sorption tests were carried out at a gel particles–solution loading ratio of 7 kg/m^3 and an initial metal concentration of 5×10^{-3} kmol/m^3. In the desorption tests the gel particles that had previously sorbed lanthanum ions were mixed with 0.1 kmol/m^3 HCl solution as an eluting solution. The lanthanum in aqueous solution is found to be sorbed by the gel particles, and the sorption process attains

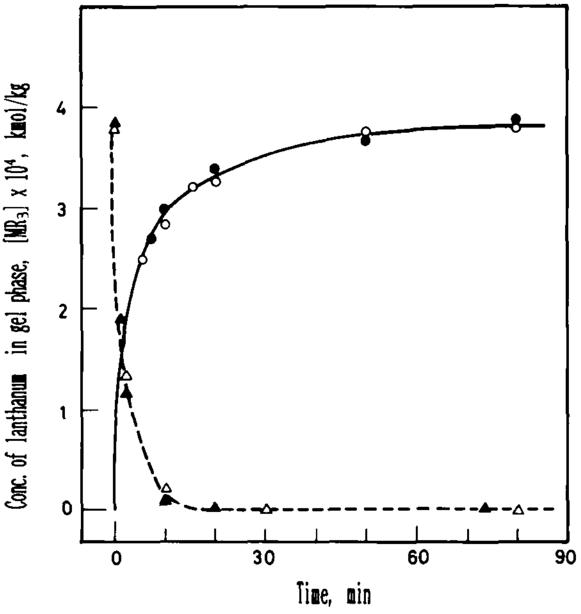

FIG. 2 Sorption and desorption behavior of lanthanum by alginic acid gel particles at 25°C and a gel particles–solution loading ratio (W/V) of 7 kg/m^3. (○) The 1st sorption test, (●) the 5th sorption test, (△) the 1st desorption test, (▲) the 5th desorption test.

equilibrium within about 60 minutes. All of the lanthanum sorbed by the gel particles is completely released into the solution by shaking within 20 minutes, suggesting that sorption–desorption is a reversible process. Thus efficient desorption of metal and regeneration of gel particles are easily achieved by using a dilute HCl solution. The sorption–desorption test for lanthanum was repeated five times to investigate the chemical stability of alginic acid gels. As shown in Fig. 2, the resorption capacity of the gel particles does not lower even in the fifth sorption test. This demonstrates that the gel particles of alginic acid can be reused to collect metal ions.

To obtain information on the stoichiometric relationship in the present biosorption system, the pH of the solution before and after the sorption of zinc and cadmium was measured. It is evident from Fig. 3 that the number of moles of H^+ ions released from the gel particles is two times that of the divalent metal ions sorbed. This result indicates that the sorption of metal ions by alginic acid takes place according to ion-exchange Reaction (1).

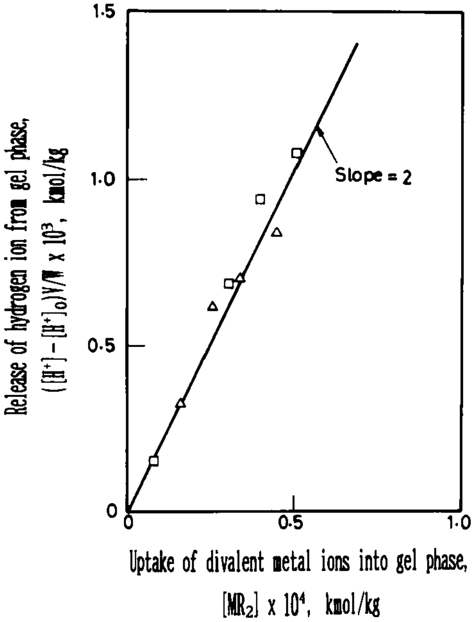

FIG. 3 Relationship between divalent metal ion uptake and hydrogen ion release at 25°C, initial liquid-phase metal concentration C_{M0} = 5.0×10^{-4} to 5.0×10^{-3} kmol/m^3, initial pH 5.5–6.2, and gel particles–solution loading ratio (W/V) = 2.5–5 kg/m^3: (□) cadmium, (△) zinc.

Evaluation of Maximum Sorption Capacity and Distribution Equilibrium Constants

Sorption equilibrium data obtained for lanthanum were used to evaluate the initial concentration Q_{HR} of functional groups in the gel particles. Figure 4 shows the experimental data plotted according to Eq. (7). The data points fall on a straight line regardless of the composition of the solution. This indicates the validity of the assumed distribution equilibrium for the present system. The maximum sorption capacity Q_{HR} of the alginic acid gel particles was evaluated as 3.78×10^{-3} kmol/kg dry gels

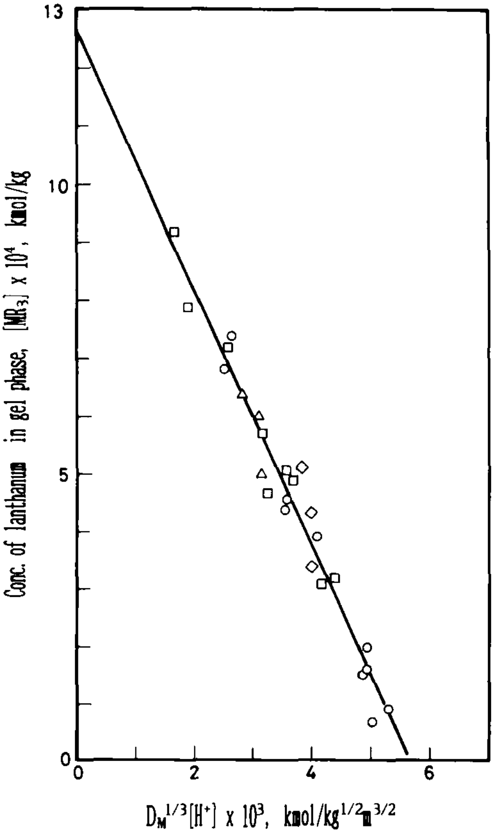

FIG. 4 Graphic evaluation of maximum sorption capacity Q_{HR} of alginic acid gel particles: (○) $C_{M0} = 1.0 \times 10^{-3}$ kmol/m^3, $W/V = 1$–5 kg/m^3, equilibrium pH 1.93–2.84; (◇) $C_{M0} = 2.5 \times 10^{-3}$ kmol/m^3, $W/V = 2.5$–5 kg/m^3, equilibrium pH 2.27–2.44; (□) $C_{M0} = 5.0 \times 10^{-3}$ kmol/m^3, $W/V = 1$–5 kg/m^3, equilibrium pH 2.01–3.10; (△) $C_{M0} = 2.5 \times 10^{-2}$ kmol/m^3, $W/V = 2.5$–5 kg/m^3, equilibrium pH 1.95–2.04.

from the intercept of the straight line. Similar plots of experimental data for zinc and cadmium showed that the gel particles have a maximum sorption capacity of 3.78×10^{-3} kmol/kg dry gels.

The relationship of the distribution ratio D_M to the concentration ratio $\overline{[HR]}/[H^+]$ was examined to test the correspondence between Eq. (4) and the experimental data obtained for lanthanum. The data from Fig. 4 are replotted as a log-log plot of D_M versus $\overline{[HR]}/[H^+]$ in Fig. 5. To calculate the abscissa value of $\overline{[HR]}/[H^+]$, the equilibrium concentration $\overline{[HR]}$ was determined from Eq. (5) by using the evaluated Q_{HR} value. It is evident from Fig. 5 that for lanthanum, all the observed distribution ratios are well correlated to a straight line with a slope of 3.0. The intercept of

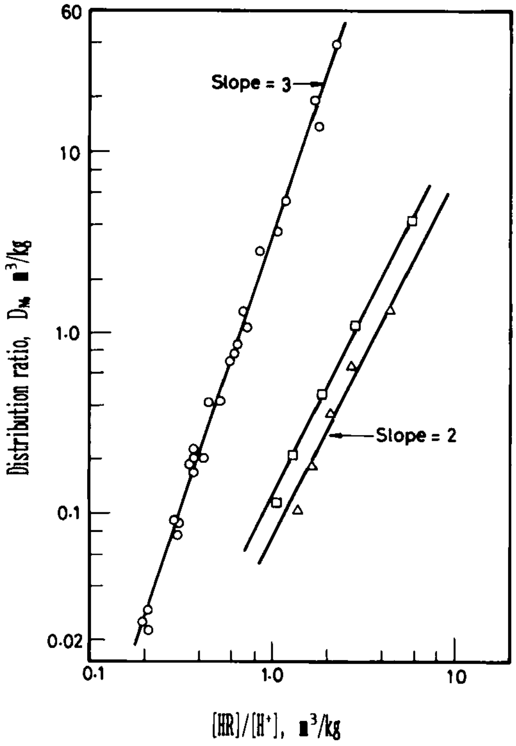

FIG. 5 Correlation for observed distribution ratios D_M of lanthanum, cadmium, and zinc at 25°C: (○) lanthanum, W/V = 1–5 kg/m³, equilibrium pH 1.93–3.10; (□) cadmium, W/V = 2.5–5 kg/m³, equilibrium pH 2.37–3.23; (△) zinc, W/V = 2.5–5 kg/m³, equilibrium pH 2.44–3.10.

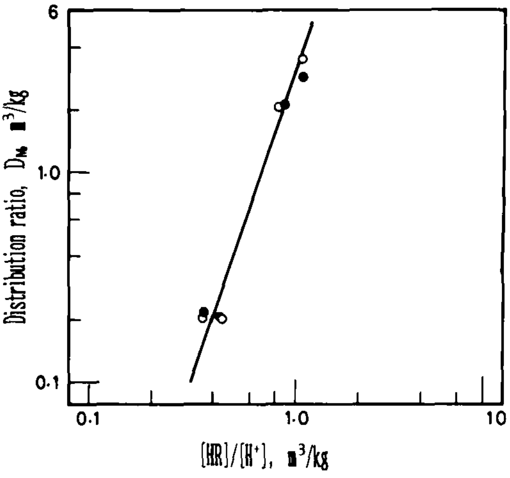

FIG. 6 Effect of temperature on distribution ratio D_M of lanthanum at initial liquid-phase metal concentration $C_{M0} = (1.0\text{–}5.0) \times 10^{-3}$ kmol/m³, equilibrium pH 2.36–2.71, and gel particles–solution loading ratio (W/V) of 1–2 kg/m³: (○) 15°C, (●) 35°C. The solid line represents the data points at 25°C.

the line yields the distribution equilibrium constant K_M of 3.4 kg²/m⁶ for lanthanum. The observed effect of the $\overline{[HR]}/[H^+]$ value on the distribution ratio is consistent with the theoretical prediction from Eq. (4).

The distribution ratios measured for zinc and cadmium are plotted against $\overline{[HR]}/[H^+]$ on a log-log scale in Fig. 5. The equilibrium concentration $\overline{[HR]}$ of free functional groups in the gel phase was determined from Eq. (5) by using the evaluated value of Q_{HR}. The data points for each metal are well correlated by a straight line with a slope of 2.0, indicating that the divalent cations Zn^{2+} and Cd^{2+} in the liquid phase exchange with the H^+ ions in the gel phase according to Reaction (1). The different intercepts of the lines correspond to the different values of the distribution equilibrium constant K_M. The K_M values evaluated from the intercepts of these lines were 0.074 kg/m³ for zinc and 0.125 kg/m³ for cadmium. The difference in the equilibrium constant appears to permit the mutual separation of these metals by the gel particles of alginic acid.

Figure 6 compares the lanthanum distribution ratios D_M measured at 15 and 35°C. The solid line represents the distribution ratio observed at 25°C. The temperature dependency of the distribution equilibrium is found to be of little importance in such a temperature range.

Comparison of Sorption Properties with Various Polymers

Some previous data on the sorption equilibria of zinc, cadmium, and lanthanum for aqueous solutions by natural and synthetic polymers (1, 2, 12–17) are shown in Table 1, along with the present experimental data for alginic acid gel particles. No data have been published on the sorption of lanthanum by natural polymers. The bark, the peanut skins, and the fish scales are effective sorbents for heavy metals. These natural materials contain significant amounts of tannin and proteins which are the major polymers governing their sorption ability. Early work indicated that phenolic, hydroxyl, amino, imidazole, and guanidino groupings in the tannin and the proteins are capable of forming complexes with metal ions (6, 12, 13). Chitin is a natural polymer found in lower animals and fungi, and chitosan is the deacetylated derivative of chitin. As shown in Table 1, chitosan has a high sorption ability compared with chitin. Muzzarelli (1) demonstrated that chitosan exhibits an excellent collection ability for transition metal ions because of its high amino groups content. Chitin and

TABLE 1

Sorption of Zinc, Cadmium, and Lanthanum from Aqueous Solutions by Various Polymers

Sorbent	Metal	Temperature (°C)	Initial concentration of metal in solution (kg/m^3)	Sorbent–solution loading ratio (kg/m^3)	Amounts of metal sorbed (g/kg)	Distribution ratio D_M (m^3/kg)
Bark (redwood) (12)	Zn(II)	—	0.0319	10	2.35	0.280
	Cd(II)	—	0.056	10	4.75	0.558
Bark (redwood) (13)	Cd(II)	—	0.10	10	6.8	0.212
Peanut skins (13)	Cd(II)	—	0.10	10	7.0	0.233
Fish scales (14) (porgy)	Zn(II)	25	1.0	10	17.6	0.0213
	Cd(II)	25	1.0	10	44.5	0.0802
Chitin (14)	Zn(II)	25	1.0	10	15.8	0.0118
	Cd(II)	25	1.0	10	40.1	0.0669
Chitosan (14)	Zn(II)	25	1.0	10	20.0	0.0250
	Cd(II)	25	1.0	10	54.3	0.119
Chitosan (1)	Zn(II)	—	0.0288	4	0.662	0.05 (pH 2.5)
Chitosan (2)	Zn(II)	—	1.31	10	21.6	0.0198
	Cd(II)	—	2.25	10	45.0	0.250
Chelating resin (15)	Cd(II)	30	2.81	5	33.2	0.0126 (pH 2.0)
	Cd(II)	30	2.81	5	96.3	0.0415 (pH 4.0)
Chelating resin (16)	Zn(II)	25	0.0654	5	11.3	1.26 (pH 2.0)
	Zn(II)	25	0.0654	5	12.3	26.2 (pH 2.8)
Chelating resin (17)	La(III)	25	0.138	5	2.36	0.0186 (pH 2.0)
Alginic acid (present work)	Cd(II)	25	0.562	2.5	55.83	0.115 (pH 2.6)
	Cd(II)	25	0.0619	2.5	18.2	1.11 (pH 2.9)
	Zn(II)	25	0.0343	2.5	4.42	0.190 (pH 2.4)
	Zn(II)	25	0.327	2.5	28.4	0.105 (pH 2.7)
	Zn(II)	25	0.0343	5	5.45	0.757 (pH 2.9)
	La(III)	25	0.138	5	12.8	0.170 (pH 2.0)

chitosan are a natural chelating polymer containing amino groups, whereas algnic acid, which is the subject of this work, is a natural chelating polymer containing carboxyl groups. The sorption ability of alginic acid gels is similar in magnitude to that of chitosan, although the distribution ratio is markedly affected by the free functional group concentration in the sorbent and the pH of the solution. Moreover, the distribution ratios of cadmium and lanthanum for alginic acid are relatively higher than for chelating resins synthesized for the selective separation of metal ions (15–17).

With respect to the maximum sorption capacity, the synthetic chelating resins have a cation-exchange capacity in the range of 1.4×10^{-3} to 4.3×10^{-3} kmol/kg resin (15–17). It is generally accepted that commercial cation-exchange resins have a maximum sorption capacity of approximate 5×10^{-3} kmol/kg resin. However, little information is available on the maximum sorption capacity of natural materials, except that the mercury-binding capacity of onion skins is 1.46×10^{-4} kmol/kg (3). The gel particles of alginic acid compare favorably with the synthetic resins in respect to their maximum sorption capacity.

CONCLUSIONS

The gel particles of alginic acid are capable of collecting zinc, cadmium, and lanthanum from aqueous solutions. The efficient desorption of the metals collected and the regeneration of the biopolymer gels can be achieved by using a dilute HCl solution of 0.1 kmol/m^3. The resorption capacity of the gels does not decrease during repeated sorption–desorption cycling. The distribution ratios of the individual metals between the gel and liquid phases were measured by a batchwise method, and the equilibrium data obtained at 25°C were analyzed with Eqs. (4) and (7). The gel particles were found to have a high sorption capacity of 3.78×10^{-3} kmol/kg. The distribution equilibrium constants were 0.074 kg/m^3 for zinc, 0.125 kg/m^3 for cadmium, and 3.4 kg^2/m^6 for lanthanum. The effect of temperature on the distribution equilibrium for lanthanum was found to be of little importance in the range from 15 to 35°C.

SYMBOLS

C_M	total concentration of metal in liquid phase (kmol/m^3)
C_{M0}	initial concentration of metal in liquid phase (kmol/m^3)
$\overline{C_M}$	total concentration of metal in gel phase (kmol/kg)
D_M	distribution of ratio of metal (m^3/kg)
$\overline{[HR]}$	concentration of free functional groups HR in gel phase (kmol/kg)

K_M	equilibrium constant for Eq. (1), $(\text{kg/m}^3)^{n-1}$
n	charge on metal ions
$[M^{n+}]$	concentration of metal ions M^{n+} in liquid phase (kmol/m^3)
$\overline{[MR_n]}$	concentration of metal in gel phase (kmol/kg)
Q_{HR}	initial concentration of functional groups in gel phase (kmol/kg)
V	volume of liquid (m^3)
W	weight of dry gel particles (kg)

ACKNOWLEDGMENTS

This research was supported in part by a Grant-in-Aid for Scientific Research (No. 62550708) from the Ministry of Education, Science and Culture, Japan. We wish to thank Mr. Takashi Goto and Mr. Jiro Nakanishi, Santoku Metal Industry Co., Ltd., Kobe, Japan, for supplying the lanthanum oxide. We also acknowledge Mr. Syun-ichiro Yamagishi, Kibun Food Co., Ltd., Osaka, Japan, for supplying the sodium alginate.

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Received by editor August 3, 1992