  Bull. Chem. Soc. Jpn., 57, 2055—2059 (1984)

Applicability of a New Adsorption Isotherm Equation and Adsorption Abilities of Commercial Chelating Resins for Single Metal Ions in Acidic Solution

Kohei URANO,* Veerapan CHANYASAK, Nobuhiko FUJII, and Toshiaki YUKAWA
Department of Safety and Environmental Engineering, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240
(Received December 8, 1983)

Adsorption isotherms for single metal ions (Ca^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, or Pb^{2+}) in acidic solutions at 25 °C on 9 types of commercial chelating resins were obtained. The results could all be expressed by the isotherm equation, $Q=Q_{max}/(1+AC_M^{-\alpha}C_H^{\beta})$, reported in the preceding paper. The parameters α and β, which indicate respectively the influences of concentrations of metal ion (C_M) and hydrogen ion (C_H) on the adsorption capacities (Q), were discussed in relation to the properties of the chelating resins and the metal ions.

Chelating resins have been used for the removal and the recovery of metals from water and also for the concentration and analysis of trace metals.[1–4] Conventional studies on chelating resins, however, related only to those involving syntheses and examples of application under specific conditions.[5] In a previous study,[6] competitive adsorptions of metal ion and of hydrogen ion on chelating resin were investigated, and it was shown that the adsorption isotherms of single heavy metal ion in acidic solution on several systems of metal ion and chelating resin could be represented by the following equation;

$$Q = Q_{max}/(1+AC_M^{-\alpha}C_H^{\beta}). \qquad (1)$$

Here Q is an adsorption amount (m mol/g-dry resin), Q_{max} is the maximum adsorption amount which can be determined from the total ion-exchange capacity of the resin, A is a correction factor, C_M is the concentration (mol dm^{-3}) of metal ion, and C_H is the concentration (mol dm^{-3}) of hydrogen ion. α and β are parameters such that the values of $1-\alpha$ and β show the exponents of the distribution function of ligands which have various dissociation constants. However, this isotherm equation is semi-theoretical and its applicability to many systems of chelating resin and metal ion over wide concentration ranges of metal ion and hydrogen ion needs to be confirmed experimentally.

The objectives of this study are to establish the validity of the above equation for various systems of commercial chelating resins and heavy metal ions, and to estimate the adsorption abilities of commercial chelating resins for various metal ions by the values of α and β in Eq.1.

Experimental

Nine types of chelating resins were employed in this study. They were UR-10, UR-20, UR-30, UR-40, UR-50, which are

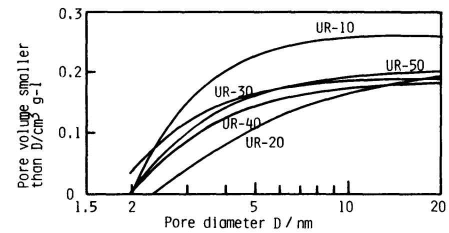

Fig. 1. Pore-size distribution of chelating resins used (I).

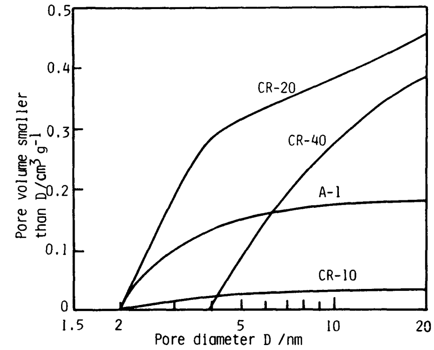

Fig. 2. Pore-size distribution of chelating resins used (II).

TABLE 1. PROPERTIES OF THE CHELATING RESINS USED

Symbol	Maker	Matrix	Main functional group	Phenolic OH meq g^{-1}	Swelling ratio (Na/H)	Surface area m^2 g^{-1}
UR-10	Unitika	Polyphenol	-N(CH$_2$COOH)$_2$	1.94	1.4	350
UR-20		Polyphenol		1.84	1.8	170
UR-30		Polyphenol		1.97	2.0	260
UR-40		Polyphenol		0.0	1.6	220
UR-50		Polyphenol		1.17	2.1	260
CR-10	Mitsubishi Chem.	Polystyrene	-N(CH$_2$COOH)$_2$	—	2.0	40
CR-20		Polystyrene	-NH(C$_2$H$_4$NH)$_n$H	—	—	—
CR-40*		Polyethylene	-CH$_2$CH$_2$NH-	—	—	—
A-1	Dow Chem.	Polystyrene	-N(CH$_2$COOH)$_2$	—	2.2	280

* gel type

products of Unitika Ltd. in Japan, CR-10, CR-20, CR-40 of Mitsubishi Chemical Industry Ltd. in Japan, and Dowex A-1 of Dow Chemical Ltd. in USA. They have various functional groups to chelate with metal ions. The properties of these resins are shown in Table 1. Their pore-size distributions which were measured by the methanol adsoption method[7]

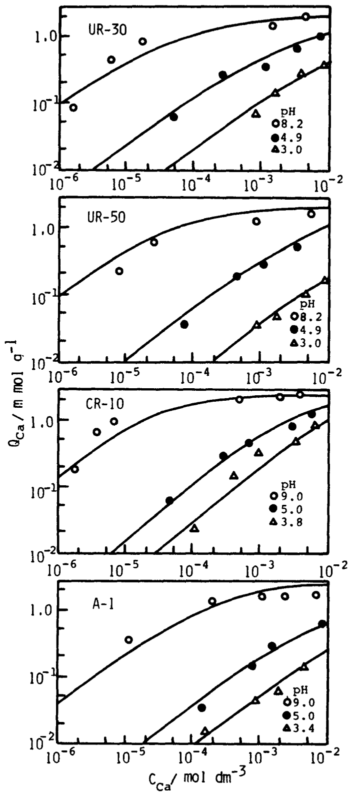

Fig. 3. Adsorption isotherms of Ca^{2+} for various resins and pH.
(Curves in Figs. 3—8 calculated by Eq. [1].)

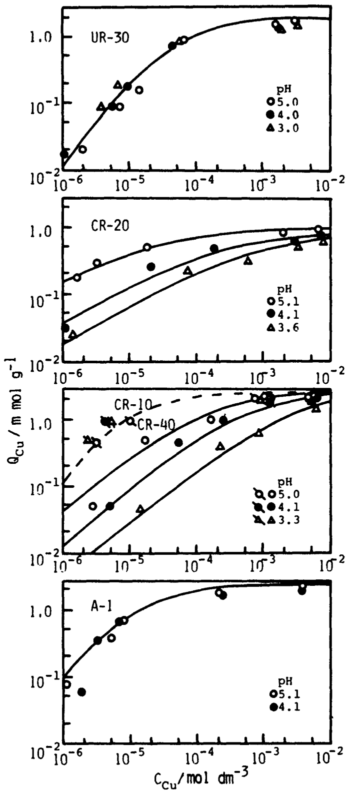

Fig. 5. Adsorption isotherms of Cu^{2+} for various resins and pH.

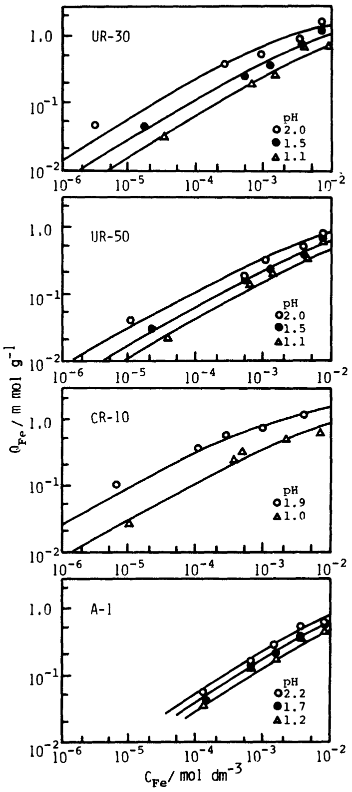

Fig. 4. Adsorption isotherms of Fe^{3+} for various resins and pH.

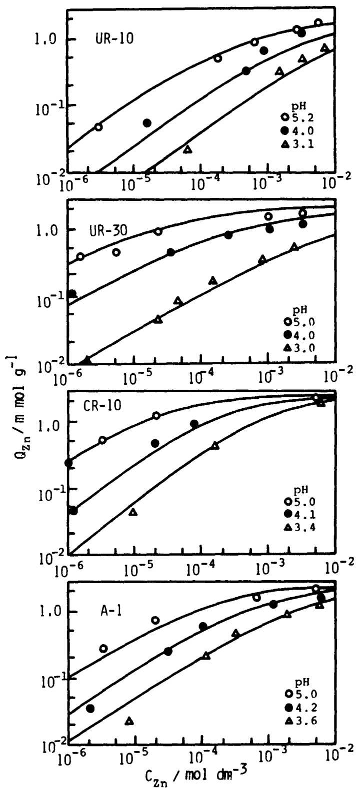

Fig. 6. Adsorption isotherms of Zn^{2+} for various resins and pH.

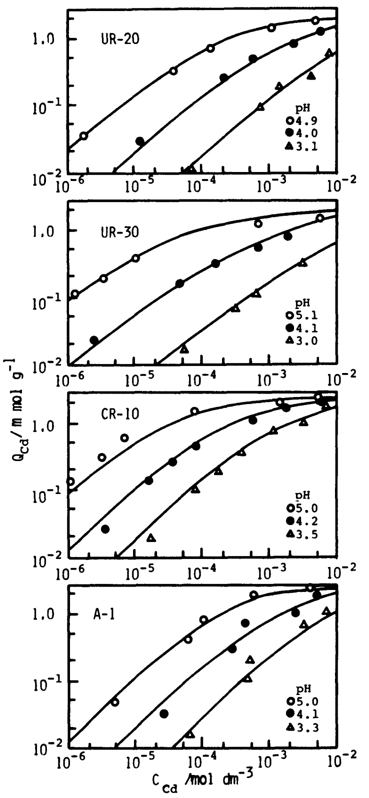

Fig. 7. Adsorption isotherms of Cd^{2+} for various resins and pH.

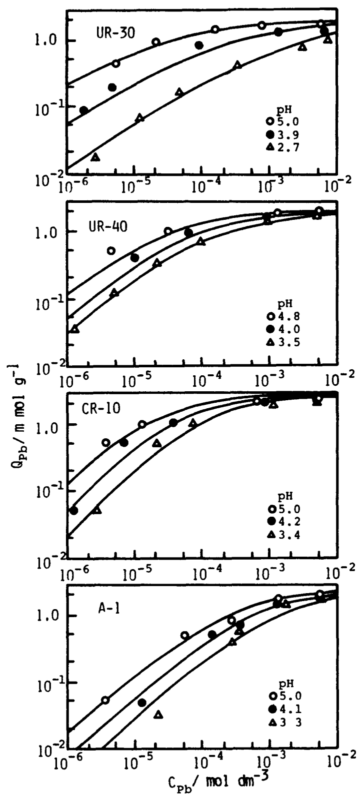

Fig. 8. Adsorption isotherms of Pb^{2+} for various resins and pH.

are shown in Figs.1 and 2. The swelling ratio corresponds to the degree of crosslinkage of the resin. Three types of UR-20 and UR-30, namely H, Ca, and Na types, were used in the experiments, but only the H type of the other resins was used.

Metal salts employed for adsorption tests were nitrates of Ca(II), Fe(III), Cu(II), Zn(II), Cd(II), and Pb(II) of reagent grade.

The methods for the pretreatments of the resins and the batchwise adsorption tests have been described in the previous paper.[6] The pH was controlled at about 3, 4, 5, 8, or 9 for the adsorption tests of Ca^{2+} about 1 or 2 for Fe^{3+}, and about 3, 4, or 5 for Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}. The concentrations of Ca^{2+} and Fe^{3+} were measured by an atomic absorption flame spectrophotometer, Model AA-610 of Shimadzu Co., and the concentrations of Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} were measured by an anodic stripping voltametric analyzer, Model AS-01 of Mitsubishi Chemical Industry Ltd.

Results and Discussion

Applicability of the Adsorption Isotherm Equation. Adsorption isotherms of each metal at 25 °C are shown in Figs. 3—8, respectively. The curves in these figures were calculated from Eq.1, and the plots show the measured data. All the measured data fitted approximately on the calculated curves. Consequently, it is confirmed that the isotherm Eq.1 can be applied generally for the various systems of commercial chelating resin and metal ion over a wide ranges of pH and concentration of the metal ion. The values of the parameters of Eq.1 for all the tested systems are listed in Table 2.

Variation of α and β with Systems of Chelating Resin and Metal Ion. Variations of the values of α and β, which show respectively the influences of C_M and C_H on Q, with the chelating resins, are discussed for each metal ion.

Calcium Adsorption: The α values of UR-10, UR-20, and UR-30 which have many phenolic OH groups are 0.66 ± 0.03 for Ca^{2+}, whereas for UR-40, UR-50, CR-10, and Dowex A-1 which have few or no phenolic OH group, the α values are 0.81 ± 0.06. The influence of the phenolic OH group on the adsorption of Ca^{2+} was greater than on the adsorption of the other heavy metal ions. This difference may be attributed to the high ionization ratio of the phenolic OH group at the higher pH values in the adsorption tests of Ca^{2+}. The β values for Ca^{2+} show only a small variation among the chelating resins. However, resins with higher degrees of crosslinkage tend to have smaller β values.

Iron (III) Adsorption: Fe^{3+} adsorbed slightly on CR-20 and CR-40 which have amino groups. For all the other resins, the α values for Fe^{3+} are 0.60 ± 0.06. Except for Dowex A-1 whose β value is 0.30, the β values of Fe^{3+} are 0.57 ± 0.09. The reason for the small β for Dowex A-1 may be because Dowex A-1 has various functional groups. Compared to CR-10, which has similar resin matrix to Dowex A-1 but only iminodiacetate functional group, Dowex A-1 has also smaller β values for other metals. In other words, more metals adsorbed on Dowex A-1 at low pH, though less adsorbed on Dowex A-1 than on CR-10 at normal pH.

Copper Adsorption: The adsorption of Cu^{2+} was specific and different from those of the other heavy metal ions. Many chelating resins could adsorb much Cu^{2+} at concentration higher than 10^{-3} mol dm^{-3}, but the adsorptions at the lower concentration range varied

TABLE 2. PARAMENTERS OF Eq. [1] OBTAINED BY EXPERIMENTS

Metal	Resin	Q_{max}	A	α	β
Ca^{2+}	UR-10	2.0	4.6	0.64	0.30
	UR-20	2.0	1.8	0.66	0.36
	UR-30	2.0	2.6	0.69	0.40
	UR-40	2.0	0.87	0.80	0.41
	UR-50	2.0	13	0.75	0.53
	CR-10	2.5	1.6	0.87	0.47
	A-1	2.5	5.1	0.75	0.38
Fe^{3+}	UR-30	2.0	0.46	0.63	0.65
	UR-50	2.0	0.73	0.58	0.48
	CR-10	2.5	0.48	0.55	0.53
	A-1	2.5	0.43	0.66	0.30
Cu^{2+}	UR-10	2.0	0.19	0.67	0.28
	UR-20(H)	2.0	2.0×10^{-7}	1.6	0.0
	UR-20(Ca)	2.0	5.0×10^{-6}	1.6	0.0
	UR-30(H)	2.0	1.0×10^{-5}	1.2	0.0
	UR-30(Na)	2.0	1.0×10^{-5}	1.2	0.0
	UR-40	2.0	2.3×10^{-3}	0.56	0.0
	UR-50	2.0	2.0×10^{-2}	0.62	0.26
	CR-10	2.5	1.7×10^{-7}	1.4	0.0
	CR-20	1.0	6.8	0.56	0.68
	CR-40	2.5	0.44	0.80	0.53
	A-1	2.5	3.4×10^{-6}	1.2	0.0
Zn^{2+}	UR-10	2.0	2.7	0.70	0.52
	UR-20(H)	2.0	7.0	0.82	0.95
	UR-20(Ca)	2.0	1.2	0.80	0.60
	UR-30(H)	2.0	18	0.57	0.78
	UR-30(Na)	2.0	24	0.58	0.71
	UR-40	2.0	0.96	0.28	0.23
	UR-50	2.0	17	0.67	0.85
	CR-10	2.5	6.0	0.76	0.87
	CR-40	2.5	116	0.49	0.51
	A-1	2.5	8.6	0.65	0.69
Cd^{2+}	UR-10	2.0	44	0.72	0.69
	UR-20(H)	2.0	46	0.84	0.97
	UR-20(Ca)	2.0	61	0.84	0.94
	UR-30(H)	2.0	27	0.71	0.88
	UR-30(Na)	2.0	80	0.72	0.80
	UR-40	2.0	24	0.86	1.0
	UR-50	2.0	47	0.68	0.80
	CR-10	2.5	20	0.86	1.0
	CR-20	1.0	0.23	0.86	0.20
	CR-40	2.5	3.1	0.91	0.50
	A-1	2.5	24	0.88	0.89
Pb^{2+}	UR-10	2.0	0.90	0.56	0.31
	UR-20(H)	2.0	7.3×10^{-2}	0.96	0.68
	UR-20(Ca)	2.0	1.2×10^{-2}	0.96	0.40
	UR-30(H)	2.0	0.76	0.63	0.55
	UR-30(Na)	2.0	1.3	0.62	0.50
	UR-40	2.0	5.0×10^{-2}	0.80	0.48
	UR-50	2.0	0.64	0.66	0.56
	CR-10	2.5	8.4×10^{-3}	0.94	0.46
	CR-20	1.7	4.9	0.99	0.55
	CR-40	0.7	0.45	1.1	0.47
	A-1	2.5	9.0×10^{-2}	0.84	0.38

widely with different resins. Therefore, the α values for Cu^{2+} vary widely with the chelating resins. The β values for Cu^{2+} are very small for most of the resins except for CR-20 and CR-40 which have amino functional groups. Two resins, CR-20 and CR-40, adsorb Cu^{2+} selectively, because N–O ligands form complexes with Cu^{2+} easily. However, the values of the parameters A, α, and β for CR-20 and CR-40, which have different a resin matrix but similar functional group, are very different form each other. Further, it was found that the α values of UR-20 for Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} were larger than those of the other resins of the UR series. The reason is unknown, though the pore-size distribution of UR-20 was different from those of the other resins.

Zinc Adsorption: The α and β values for Zn^{2+} show large variations with the chelating resins. The α values of the UR series resins for Zn^{2+} do not depend on the amount of phenolic OH group. The α values of UR-20 or UR-30 of different ion types, namely H, Na, and Ca types, for Zn^{2+} are slightly different, but the β values of these different type resins decreased in the following order: H type>Na type>Ca type. In the cases of the Ca type resins, Ca^{2+} ion which was released with adsorption of H^+ might be adsorbed competitively with Zn^{2+}, as a result, the apparent β values are smaller than those of the other types. However, in the cases of the Na type resins, the released Na^+ might be adsorbed much less than Zn^{2+}. The reason for the smaller β values of the Na type resins than the H type resins might be that Na^+ in the resins became difficult to release due to shrinking of the Na type resins with the adsorption of H^+. It was also found that the β values for Cd^{2+} and Pb^{2+} of different type resins varied in the same order as in the case of Zn^{2+}.

Cadmium Adsorption: The α values of the UR series resins for Cd^{2+} do not depend on the amounts of phenolic OH group, but the α values of UR-40 having no phenolic OH group are larger than the other resins of UR series. The β values of CR-20 and CR-40, which have amino group, for Cd^{2+} are smaller than those of the other resins. The β value of UR-10 with high degree of crosslinkage for Cd^{2+} is slightly smaller than those of the other resins of UR series.

Lead Adsorption: As is in the case of Cd^{2+}, the α values for Pb^{2+} can be divided into two groups; (1) UR-10, UR-30, and UR-50 and (2) the other resins. The β value of UR-10 for Pb^{2+} is also smaller than the values of the other resins, this is similar to the case of Cd^{2+}. As mentioned previously, the β value of UR-20 is larger than the values of the other resins.

Order of β Values: The β values of various chelating resins increase in the order: $Cu^{2+}<Ca^{2+}<Pb^{2+}<Fe^{3+}<Zn^{2+}<Cd^{2+}$. This order, except for Ca^{2+} whose adsorption tests were carried out at higher pH than the others, is in opposite order to the stability constants of ethylenediaminetetraacetate with these metal ions. The reason for the deviation of Ca^{2+} adsorption may be that the phenolic OH group of the resins of UR series influences the adsorption at the higher pH range.

References

1) M. I. Abdullah and L. G. Royle, *Anal. Chim. Acta*, **58**, 283 (1972).

2) J. Digman Jr., K. M. Gloss, E. A. Milano, and S. Sigga, *Anal. Chem.*, **46**, 774 (1974).

3) P. Burba and K. H. Lieser, *Angew. Makromol. Chem.*, **64**, 197 (1977).

4) K. Urano and N. Fujii, *Mizushorigijutsu*, **22**, 1031 (1981).

5) K. Urano and N. Fujii, *Mizushorigijutsu*, **23**, 3 (1982).

6) K. Urano, V. Chanyasak, and N. Fujii, *J. Colloid Interface Sci.*, **82**, 251 (1981).

7) K. Urano, *Hyomen*, **13**, 738 (1975).