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Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process

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Abstract

Copper and zinc removal from aqueous solution by chelating resin was investigated theoretically and experimentally in the present study. A multistage process was proposed as an alternative for enhancement of the heavy removal of the single-stage process. Heavy metal mass balance equations with empirical Freundlich adsorption isotherm were developed to represent the multistage process and the theoretical model permits determination of the inter-stage heavy metal concentrations and the total amount of chelating resin required for achieving a desired level of heavy metal removal. Optimization of the linearized theoretical model shows that equal division of the total amount of chelating resin among all stages of the multistage process yields the best results in terms of saving of chelating resin for a given heavy metal removal or enhanced heavy metal removal for a given total amount of chelating resin. Experimental tests were also conducted to establish the equilibrium adsorption of heavy metal by the chelating resin and to empirically verify the advantages of the multistage adsorption process. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heavy metals; Chelating resin; Multistage adsorption process; Freundlich adsorption isotherm

1. Introduction

Removal of heavy metals from aqueous solution is necessary because of frequent appearance of these heavy metals in wastewaters from many industries, including electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing industries. This problem has received considerable amount of

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attention in recent years due primarily to concern that those heavy metals in wastewater can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [1,2]. Hence, removal of heavy metals from industrial wastewater is of practical interest.

Many physicochemical methods have been developed for heavy metal removal from aqueous solution, including chemical coagulation, adsorption, extraction, ion exchange and membrane separation process [1,3–6]. Among these methods, ion exchange is a highly popular one and has been widely practiced in industrial wastewater treatment process. The chelating resin employed in the ion exchange processes in general is non-selective and has affinity for alkaline earth, alkali and heavy metals [1,3]. Improvement of the resin selectivity for heavy metal involves introducing specialty functional groups onto the polymer matrix of the ion exchange resin [7,8].

The operation of ion exchange for heavy metal removal is usually carried out in a batch vessel or packed column. The batch ion exchange process in a single vessel offers the advantages of high operating flexibility. However, a single-stage ion exchange process seldom achieves the desired level of heavy metal removal [9]. As an alternative, a multistage ion exchange process is more desirable, leading to either enhanced heavy metal efficiency or saving of significant amount of ion exchange resin. The objective of this study is to investigate the multistage ion exchange process of chelating resin. Stagewise mass balance equations are developed that allow determination of optimum allocation of ion exchange resins among the adsorption stages. To verify the theoretical developments, experimental tests are also conducted to examine the heavy metal removal efficiencies. The theoretical mass balance equations developed in this work can be of significant value to practical design of the multistage ion exchange process.

2. Theoretical adsorption model

Fig. 1 graphically demonstrates the general adsorption capacity and heavy metal removal as a function of the amount of chelating resin employed in a single-stage adsorption process. The figure shows that the resin adsorption capacity (mg heavy metal/g resin) decreases and the heavy metal removal increases with an increase in the amount of chelating resin. To achieve a good heavy metal removal from aqueous solution, a large amount of chelating resin is required, leading to low utilization of chelating resin due to its low adsorption capacity. To maintain both good heavy metal removal and resin adsorption capacity, a multistage adsorption process can offer a good choice. In this process, the total amount of chelating resin is allocated in proper proportions to different stages and hence a higher adsorption capacity can be realized in each stage because of smaller amount of chelating resin used. In the following sections, theoretical modeling and experimental verifications of the multistage ion exchange process will be elaborated.

2.1. Single-stage adsorption process

The single- and multi-stage adsorption processes are illustrated in the top and bottom graphs of Fig. 2, respectively. In Fig. 2(b), $C_{e(j-1)}$ denotes the heavy metal concentra-

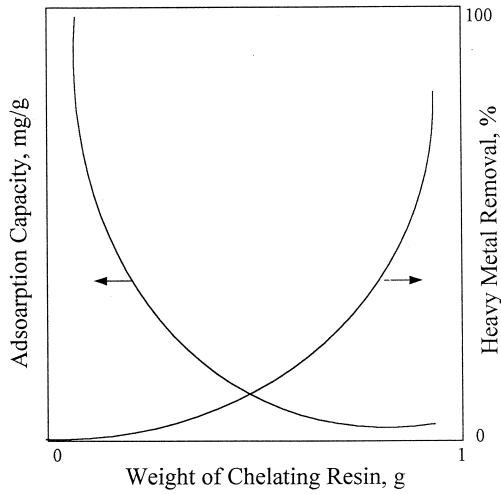
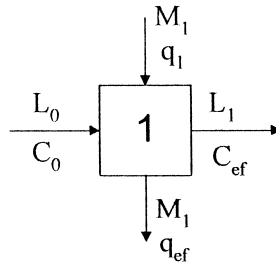
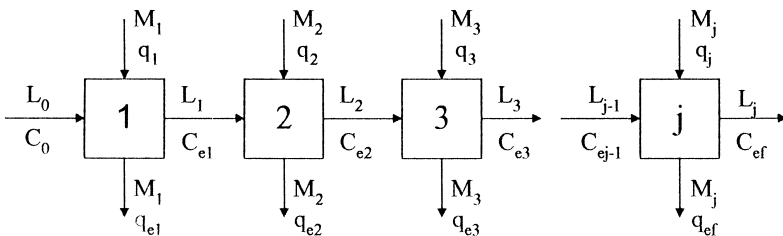


Fig. 1. The adsorption capacity and heavy metal removal vs. the amount of chelating resin.



(a) Single-Stage Process



(b) Multistage Process

Fig. 2. Schematics of the single- and multi-stage adsorption processes.

tion (mg/l) in the aqueous solution entering the j th adsorption stage, L_{j-1} and M_j are, respectively, the amounts of aqueous solution (l) and chelating resin (g) entering the same stage, and q_j and q_{ej} (mg/g) represent the heavy metal concentrations of the chelating resin entering and leaving the j th stage. Assuming that fresh chelating resin is used for each stage and there is no volume change of aqueous solution for all adsorption stages, there exists

$$L_1 = L_2 = \dots = L_j = \dots = L \quad (1)$$

$$q_1 = q_2 = \dots = q_j = \dots = 0 \quad (2)$$

A heavy metal mass balance for the single-stage process yields

$$M_s(q_{ef}) = L(C_0 - C_{ef}) \quad (3)$$

or

$$q_{ef} = (C_{ef} - C_0)(-L/M_s) \quad (4)$$

where C_{ef} and M_s designate the final heavy metal concentration in equilibrium with q_{ef} and the amount of chelating resin used in the single-stage process, respectively. Eq. (4) represents the operating line of the single-stage adsorption process, as shown by the dashed straight line in the top or bottom graph of Fig. 3. The quantity $(-L/M_s)$ in Eq. (4) is the slope (m_s) of this operating line in this figure. According to this definition, Eq. (4) can be rewritten as

$$m_s = q_{ef}/(C_{ef} - C_0) \quad (5)$$

which can also be obtained graphically from Fig. 3. It is noted that the adsorption equilibrium relation between q_{ef} and C_{ef} is represented by the empirical Freundlich isotherm [4]

$$q_{ef} = KC_{ef}^{1/n} \quad (6)$$

where K and n are the constant isotherm parameters. This adsorption isotherm will be verified later in the experimental tests.

2.2. Two-stage adsorption process

For the two-stage process, the following heavy metal mass balances are obtained for each stage from the top graph of Fig. 3

$$m_1 = q_{e1}/(C_{e1} - C_0) \quad (7)$$

$$m_2 = q_{ef}/(C_{ef} - C_{e1}) \quad (8)$$

These equations are rearranged to

$$q_{e1} = (C_{e1} - C_0)(-L/M_1) \quad (9)$$

$$q_{ef} = (C_{ef} - C_{e1})(-L/M_2) \quad (10)$$

The equilibrium relations for q_{e1} vs. C_{e1} and q_{e2} vs. C_{ef} can be represented by a similar isotherm of Eq. (6). Adding Eq. (9) to Eq. (10) yields

$$q_{e1} + q_{ef} = -L[(C_{e1} - C_{e0})/M_1 + (C_{ef} - C_{e1})/M_2] \quad (11)$$

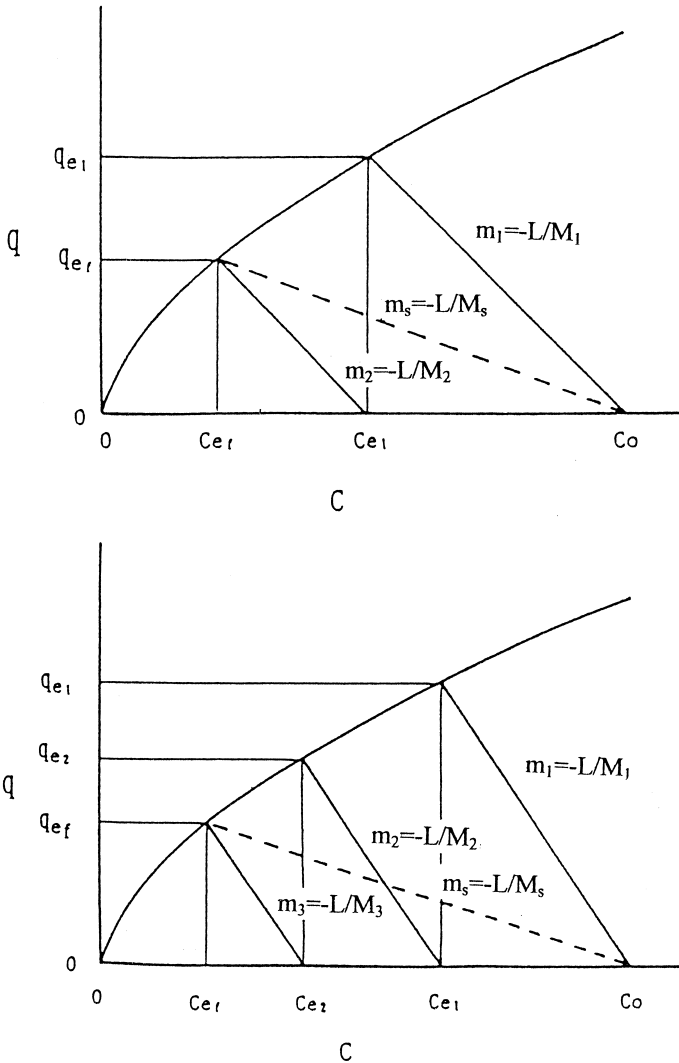


Fig. 3. Cocurrent two- and three-stage equilibrium adsorption.

The heavy metal mass balance equations established above permit theoretical determination of the optimum chelating resin allocation for each stage for a given total amount ($M_1 + M_2$) and given inlet and outlet heavy metal concentrations (C_0 and C_{ef}). To illustrate and simplify the optimization process, the Freundlich isotherm is assumed to a first-order, i.e. $n = 1$. With this assumption, the total amount of chelating resin for the two-stage process (M_d) is obtained from Eqs. (9) and (10)

$$M_d/L = (M_1 + M_2)/L = (C_{e1} - C_0)/(KC_{e1}) + (C_{ef} - C_{e1})/(KC_{ef}) \quad (12)$$

To minimize the total amount of chelating resin (M_d) required, the left-hand side quantity (M_d/L) is differentiated with respect to C_{e1} and the resulting equation is set to zero yielding

$$C_{ef} = C_{e1}^2/C_0 \quad (13)$$

Substitution of C_{ef} into M_2/L , Eq. (10), leads to

$$\begin{aligned} M_2/L &= (C_{ef} - C_{e1})/(KC_{ef}) = (C_{e1}^2/C_0 - C_{e1})/[K(C_{e1}^2/C_0)] \\ &= (C_{e1} - C_0)/(KC_{e1}) = (C_{e1} - C_0)/q_{e1} \end{aligned}$$

which, according to Eq. (9), is identical to M_1/L . Hence the optimum allocation is that the total amount of chelating resin is equally divided into two parts, i.e. $M_1 = M_2 = M_d/2$. In other words, the slopes of the two operating lines in the top graph of Fig. 3 are equal. Eq. (11) then is rearranged as

$$M_1/L = M_d/(2L) = (C_0 - C_{ef})/(q_{e1} + q_{ef}) \quad (14)$$

Noting that $m_s = (-L/M_s)$ and $M_d = 2M_1$, the ratio of the amount of chelating resin for the two-stage process (M_d) to that for the single-stage process (M_s) is obtained from Eqs. (5) and (14),

$$\begin{aligned} M_d/M_s &= 2q_{ef}/(q_{e1} + q_{ef}) = 2/(1 + q_{e1}/q_{ef}) \\ &= 2/[1 + (C_{e1}/C_0)^{1/n}/(C_{ef}/C_0)^{1/n}] \end{aligned} \quad (15)$$

It is apparent from the top graph of Fig. 3 that q_{e1} is larger than q_{ef} and hence M_d/M_s is always less than 1, implying that a saving in the total amount of chelating resin is achieved for the two-stage process over that of the single-stage process.

Since $M_1 = M_2 = M_d/2$, equating Eq. (9) to Eq. (10) and rearranging leads to

$$(1 - C_{e1}/C_0)/(C_{e1}/C_0 - C_{ef}/C_0) = (C_{ef}/C_0)^{1/n}/(C_{e1}/C_0)^{1/n} \quad (16)$$

The above equation permits determination of the inter-stage heavy metal concentration (C_{e1}/C_0) by an iterative method as a function of (C_{ef}/C_0) and n . The results are displayed in the top graph of Fig. 4. Knowing the inter-stage heavy metal concentration (C_{e1}/C_0), M_d/M_s is then generated from Eq. (15), as shown in the bottom graph of Fig. 4. Apparently, saving in the amount of chelating resin becomes increasingly more significant with a decrease in both (C_{ef}/C_0) and n .

2.3. Three-stage adsorption process

For the three-stage adsorption, it is assumed that the total amount of chelating resin is equally divided for the three stages. Invoking similar manipulations, the following equation can be established

$$M_1/L = M_t/(3L) = (C_0 - C_{ef})/(q_{e1} + q_{e2} + q_{ef}) \quad (17)$$

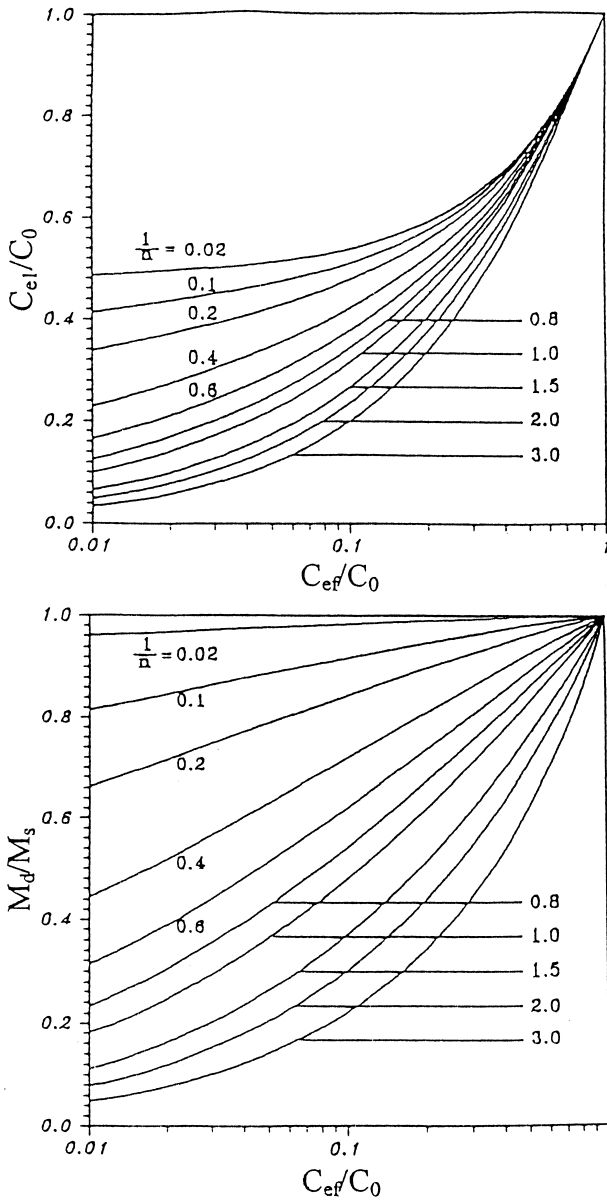


Fig. 4. The inter-stage heavy metal concentration (top) and the relative amount of resin required for the two- and single-stage processes (bottom) as a function of C_{ef}/C_0 and n .

which is similar to Eq. (14) for the two-stage process. The ratio of the total amounts of chelating resin for the three- and single-stage processes is obtained from Eqs. (3) and (17) as

$$M_t/M_s = 3q_{ef}/(q_{e1} + q_{e2} + q_{ef}) = 3/(1 + q_{e1}/q_{ef} + q_{e2}/q_{ef}) \quad (18)$$

It is apparent from the bottom of Fig. 3 that $q_{e1}/q_{ef} < 1$ and $q_{e2}/q_{ef} < 1$, hence M_t/M_s is less than one.

The equations for establishing the inter-stage heavy metal concentrations are given by

$$(1 - C_{e1}/C_0)/(C_{e1}/C_0 - C_{e2}/C_0) = (C_{e1}/C_0)^{1/n}/(C_{e2}/C_0)^{1/n} \tag{19}$$

$$(1 - C_{e1}/C_0)/(C_{e2}/C_0 - C_{ef}/C_0) = (C_{e1}/C_0)^{1/n}/(C_{ef}/C_0)^{1/n} \tag{20}$$

which allow iterative determinations of the inter-stage heavy metal concentrations (C_{e1}/C_0 and C_{e2}/C_0) as a function of (C_{ef}/C_0) and n . The results are demonstrated in the top and bottom graphs of Fig. 5. The ratio of the total amounts of chelating resin for the three-stage process becomes

$$\frac{M_t}{M_s} = \frac{3}{1 + \frac{(C_{e1}/C_0)^{1/n}}{(C_{ef}/C_0)^{1/n}} + \frac{(C_{e2}/C_0)^{1/n}}{(C_{ef}/C_0)^{1/n}}} \tag{21}$$

This ratio is shown in the top graph of Fig. 6. Again, saving in the amount of chelating for the three-stage process is seen to increase with a decrease in (C_{ef}/C_0) and n .

2.4. Infinite-stage adsorption process

According to Eq. (3), the general heavy metal mass balance can be written in the following general form

$$M/L = (1/q_{ef})(C_0 - C_{ef}) \tag{22}$$

This equation clearly shows that if $1/q_{ef}$ is plotted against $(C_0 - C_{ef})$, the total amount of chelating resin required (M/L) is represented by the rectangle formed by $1/q_{ef}$ and $(C_0 - C_{ef})$. For example, the total amount of chelating resin for the single-stage process (M_s/L) is represented by the rectangular area IJKL in the top graph of Fig. 7. For the two-stage process, the total amount of chelating resin is

$$M_d/L = (C_0 - C_{e1})/q_{e1} + (C_{e1} - C_{ef})/q_{ef} \tag{23}$$

Eq. (23) represents the sum of the rectangular areas MNKP and IOPL, resulting in a saving of chelating resin by the amount represented by the rectangle OJNM, when compared to that of the single-stage process (IJKL). Following the same argument, the amount of chelating resin for the j -stage process is given by

$$M_j/L = (C_0 - C_{e1})/q_{e1} + (C_{e1} - C_{e2})/q_{e2} + \dots + (C_{e(j-1)} - C_{ef})/q_{ef} \tag{24}$$

The bottom graph of Fig. 7 shows several rectangular areas representing the amount of chelating resin for different the j -stage processes. It is seen that as the number of stage increases, the total amount of chelating resin decreases. The extreme is reached when the number of stage becomes infinity, as represented by the dashed line in the bottom graph of Fig. 7. For this case, the total amount of chelating resin (M_∞) becomes the area

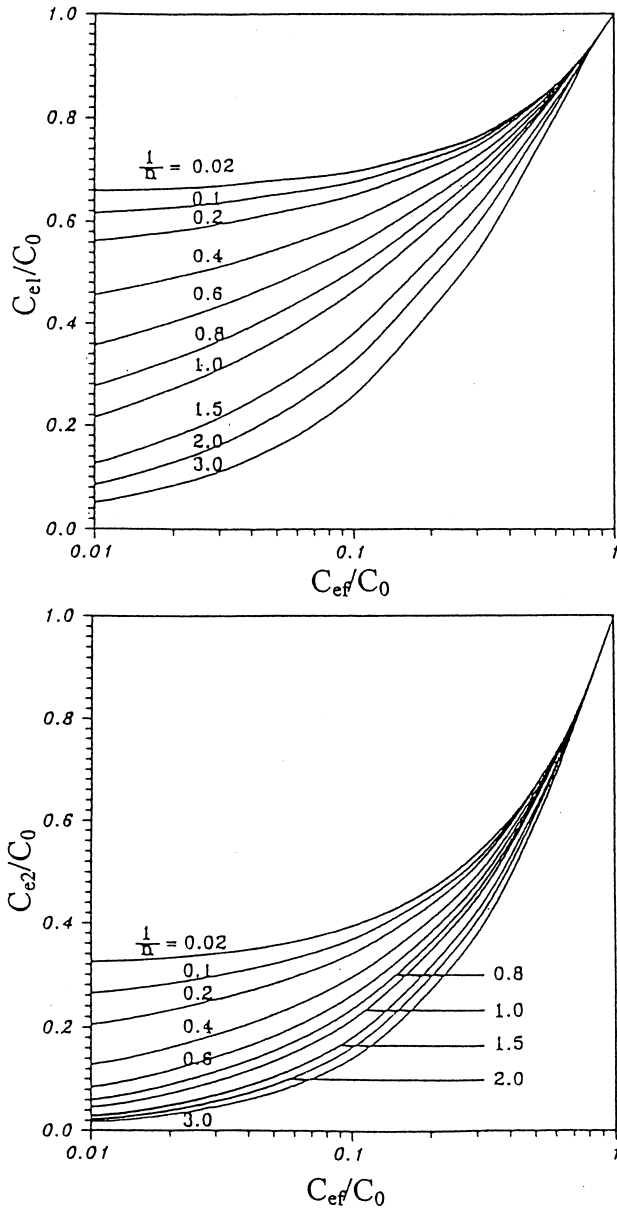


Fig. 5. The inter-stage heavy metal concentrations for the three-stage process as a function of C_{ef}/C_0 and n .

of IQKL bounded by the dashed line on the top. This amount can also be obtained by integrating the isotherm curve from C_{ef} to C_0 as follows

$$M_{\infty}/L = \text{Area IQKL} = \int_{C_{ef}}^{C_0} (1/q_e) dC \tag{25}$$

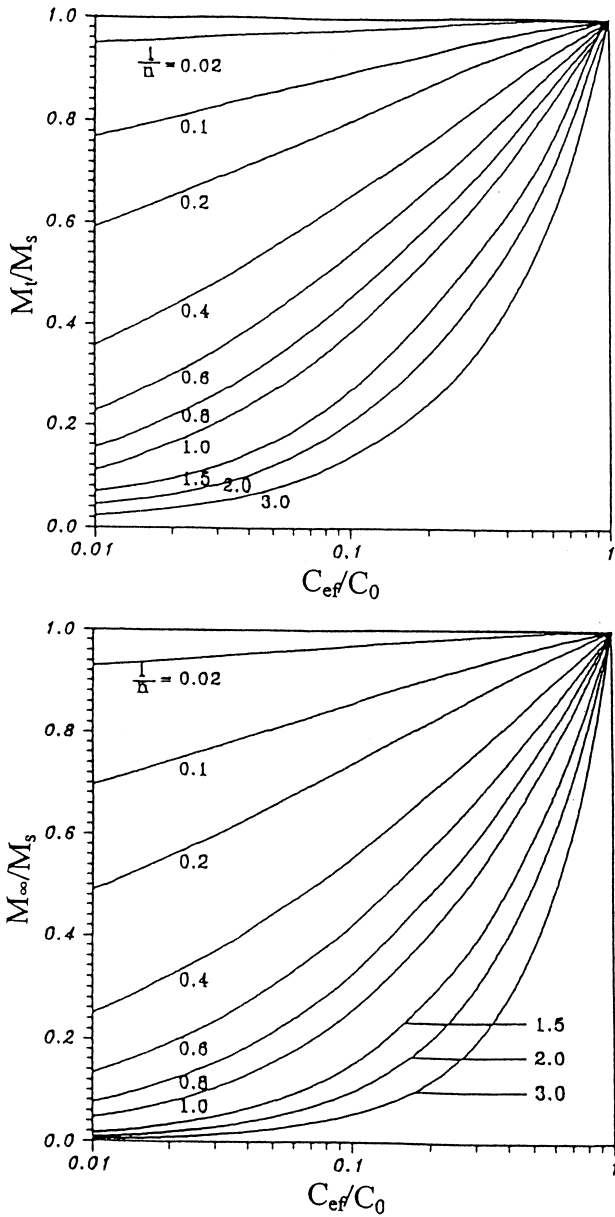


Fig. 6. The relative amounts of chelating resin required for the three-(top) and infinite-stage (bottom) processes as a function of C_{ef}/C_0 and n .

Performing the above integration using the Freundlich isotherm gives

$$\frac{M_\infty}{L} = \frac{n}{K(n-1)} \left[C_0^{(n-1)/n} - C_{ef}^{(n-1)/n} \right] \tag{26}$$

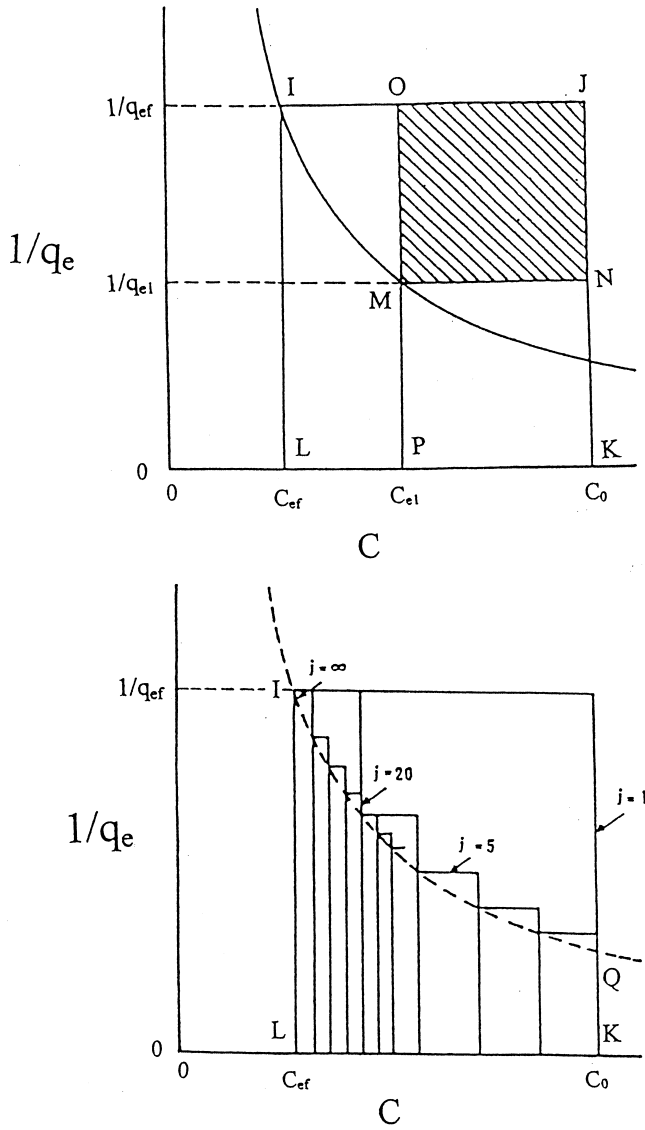


Fig. 7. Graphical representations of two-(top) and multi-stage (bottom) adsorption process.

Finally, the ratio of the amounts of chelating resin for infinite- and single-stage processes is obtained as

$$\frac{M_\infty}{M_s} = \frac{n}{n-1} \frac{[1 - (C_{ef}/C_0)^{(n-1)/n}](C_{ef}/C_0)^{1/n}}{1 - (C_{ef}/C_0)} \quad (27)$$

The above amount ratio is shown in the bottom graph of Fig. 6 as a function of (C_{ef}/C_0) and n . This represents the minimum ratio of the amounts of chelating resin that can be achieved by a multistage adsorption process.

3. Materials and methods

To verify the above theoretical developments, a series of experimental tests for the single- and two-stage adsorption processes were performed in the present study.

The chelating resin employed in this study was Amberlite IRC-718, obtained from Rohm and Haas (Philadelphia, PA). The resin is a macroporous polymer cross-linked of styrene monomer (SM) and divinylbenzene (DVB). The Na-type Amberlite IRC-718 had a size distribution of 16-40 standard mesh and its cation exchange capacity (CEC) was 1.1 meq/ml wet resin, which was quite good. According to the manufacturer, it has a high affinity for heavy metals. For pretreatment, the Amberlite IRC-718 resin was washed several times first by deionized water and by acetone to remove all impurities on its surfaces. Hexane was then used to rinse the resin several times. Finally, the resin surfaces were dried using a paper towel and the resins were stored in a desiccator.

Stock solutions with six different initial copper or zinc concentrations (maximum 200 and 100 mg/l for copper and zinc, respectively) were prepared using reagent grade copper nitrate ($\text{Cu}(\text{NO}_3)_2$) and zinc chloride (ZnCl_2), obtained from E Merck (Darmstadt, Germany). One hundred milliliters of the prepared stock were put in a flask with 0.1 g of pretreated chelating resin added. The mixture in the flask was mixed at 120 rpm by a magnetic stirrer and maintained at constant temperature (30°C) for 24 h to ensure

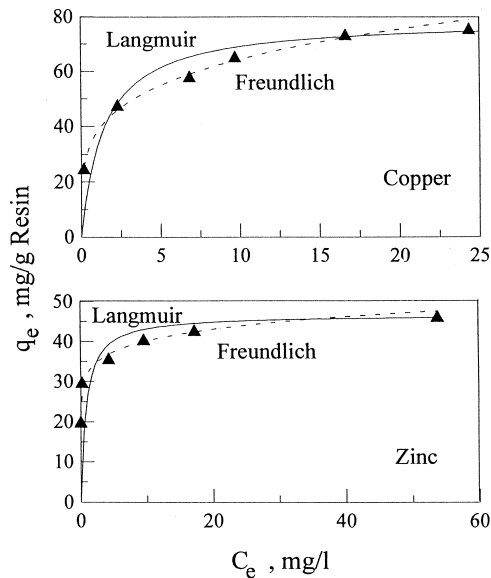


Fig. 8. Comparison of the Freundlich model fit of heavy metal adsorption isotherm by Amberlite IRC-718.

Table 1
Constant parameters of the Freundlich isotherm

Heavy metal	K	n	r^2
Copper	37.99	4.37	0.994
Zinc	31.84	9.94	0.992

adsorption equilibrium. Aqueous samples were then taken for copper or zinc concentration measurements using a GBC 932 atomic absorption spectrophotometer (GBC Scientific Equipment, Melbourne, Australia).

For single-stage adsorption test, the procedure was the same as that of the above equilibrium test except that 100 ml of 200 mg/l copper (or 100 mg/l zinc) solution and 0.2 g of pretreated chelating Amberlite IRC-718 were used. Two-stage adsorption tests were conducted in a similar fashion. 100 ml of 200 mg/l copper (or 100 mg/l zinc) solution were put in a flask and 0.1 g of pretreated chelating resin added. The mixture of the flask was mixed at 120 rpm and maintained at constant 30°C. After reaching equilibrium in 24 h, the chelating resin was separated and the copper concentration of the aqueous solution determined. To the aqueous solution, 0.1 g of fresh chelating resin was added and the test procedure repeated.

4. Results of experimental tests

Fig. 8 displayed the equilibrium adsorption of copper and zinc by the chelating Amberlite IRC-718. In this figure, the monolayer Langmuir and empirical Freundlich isotherms were employed to represent the isotherm data. It is apparent that the Freundlich isotherm describes the observed data much better than the Langmuir alternative and this justifies adoption of the former isotherm in the previous theoretical developments. The isotherm parameters for copper and zinc are listed in Table 1.

Table 2
Test results of the single- and two-stage adsorption

Heavy metal	Single-stage		Two-stage			
	Cu	Zn	First-stage		Second-stage	
			Cu	Zn	Cu	Zn
Item						
Initial conc., C_0	200	100	200	100	92.9	52.6
Amount of resin (g)	0.2	0.2	0.1	0.1	0.1	0.1
Observed C_{ef}	36.8	15.1	92.9	52.6	19.5	10.4
Calculated C_{ef}	34.8	14.6	94.3	53.8	18.4	9.2
Removal (%)	81.6	84.9	53.5	47.4	79.0	80.2
Total removal (%)					90.2	89.6

C_0 —initial heavy metal concentration (mg/l).

C_{ef} —final heavy metal concentration (mg/l).

The results for the single- and two-stage adsorption tests are shown in Table 2. Also listed in this table are the final heavy metal concentrations for each stage calculated from the theoretical model using the empirical Freundlich isotherm. The calculated heavy metal concentrations agree reasonably well with the corresponding measurements. It is further noted that the heavy metal removal of the two-stage adsorption is significantly improved when compared to that of the single-stage adsorption, 90.2% (two-stage) vs. 81.6% (single stage) for copper and 89.6% vs. 84.6% for zinc, confirming the results drawn from the theoretical developments. The improvement in the heavy metal removal for the two-stage adsorption over that for the single-stage adsorption was observed in the experimental tests to be even more pronounced if the heavy metal removal of the single-stage process is lower than 80%.

5. Conclusions

Heavy metal removal from aqueous solution by chelating resin was investigated theoretically and experimentally in a multistage process in the present work. Heavy metal mass balance equations with empirical Freundlich isotherm were developed for representing the multistage adsorption process. The mass balance equations permit theoretical determination of the inter-stage heavy metal concentrations and the amount of chelating resin required to achieve a desired heavy metal removal. Mass balance equations for the two-, three- and infinite-stage adsorption processes were adopted to illustrate the advantages of the multistage adsorption process. Optimization of linearized theoretical model indicates that equal division of the total amount of chelating resin over all stages yields the best heavy metal removal for the multistage adsorption process. Experimental tests were also conducted to establish the equilibrium adsorption isotherm and to verify the results of theoretical developments of the multistage adsorption process. Results of experimental observations show that the measured data agree well the theoretical predictions using the developed heavy metal mass balance equations.

Nomenclature

C_j	heavy metal concentration in the aqueous solution exiting the j th stage (mg/l)
C_e	equilibrium heavy metal concentration in the chelating (mg/l)
K	adsorption isotherm parameter
L	volume of aqueous solution (l)
m_j	slope of the adsorption operating line (l/g)
M_j	amount of chelating resin entering the j th stage (g)
n	adsorption isotherm parameter
q_j	heavy metal concentration in the chelating resin exiting the j th stage (mg/g resin)

subscripts

d	two-stage adsorption process
f	final stage

j	the j th adsorption stage
s	single-stage adsorption process
t	three-stage adsorption process
0	inlet condition
∞	infinite stage adsorption process

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