REMOVAL OF COEXISTING Pb^{2+} , Cu^{2+} and Cd^{2+} IONS FROM WATER BY ADDITION OF HYDROXYAPATITE POWDER

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Key Words: Adsorption, Hydroxyapatite, Batch Tank Adsorber, Rectangular Isotherm, Concentration Decay Curve, Heavy-Metal Ions Removal, Ion Exchange Selectivity, X-ray Diffraction Patterns

Removal of single, binary and ternary divalent heavy metal ions, i.e., Pb^{2+} , Cu^{2+} and Cd^{2+} , respectively, from their chloride or nitrate aqueous solutions was studied by the addition of hydroxyapatite in an agitated tank adsorber.

The isotherms for each single component were of the rectangular type, i.e., the amounts removed from aqueous phase were constant irrespective of the concentration of solutions. For binary and ternary systems, equilibrium relations were expressed in terms of selectivity coefficient.

Concentration decay curves were prepared from experimental data for comparison with theoretical calculations.

Regarding mass transfer, it was found that Pb^{2+} was collected on the apatite structure very fast, while the two other ions showed some resistances other than film diffusion resistance.

Furthermore, the apatite structure was studied by X-ray diffractometry.

Introduction

In recent years, waste-water treatment techniques have shown great progress in various aspects. Most industries are treating polluted water at their plant sites. Regarding the removal of toxic heavy-metal ions from industrial waste water, coagulative precipitation, ion exchange and reverse osmosis are generally used.⁴⁾ However, it still seems necessary to develop a new method that attains a higher removal level. As a result, various types of adsorbents or ion exchangers have been tried.

It was found that synthetic hydroxyapatite, a calcium phosphate compound, showed very high removal capacity for divalent heavy-metal ions through exchange between the Ca^{2+} ions that exist in the hydroxyapatite structure and the heavy-metal ions such as Pb^{2+} , Cu^{2+} and Cd^{2+} in water under ambient conditions.⁸⁾

This paper is aimed at extending the previous results on single heavy-metal ions removal⁹⁾ to binary- and ternary-component systems of heavy-metal ions. Binary and ternary equilibria were expressed by using selectivity coefficients and values of the mass transfer coefficient were obtained. Furthermore, the rate of mass transfer for each ion was discussed, considering film diffusion and the exchange process of ions at the sites of apatite structure. As a whole, hydroxyapatite powders seem to be useful in the removal of divalent heavy-metal ions from water.

1. Experimental

1.1 Materials

Hydroxyapatite particles, supplied by Mitsui Toatsu Chemicals, Inc., were sieved and their 150- to 200-mesh fraction was used after washing with distilled water and drying in a common drying apparatus.

Physical properties of the sample were measured by ordinary methods, i.e. the specific surface area was determined from a nitrogen adsorption method to be $5.42 \times 10^4 \text{ m}^2/\text{kg}$, and the particle density was determined to be $2.93 \times 10^3 \text{ kg/m}^3$ by a pycnometer method. The molar ratio Ca/P of the sample was reported to be 1.66.⁸⁾

1.2 Experimental procedure

Firstly, aqueous solutions containing Pb^{2+} , Cu^{2+} , or Cd^{2+} ions in the form of chloride or nitrate of various concentrations were prepared. The pH of the solution was set at about 3.0, 4.0, or 5.0, respectively, with the addition of either hydrochloric acid or nitric acid according to the anion coexisting in the solution.

The solutions thus prepared were taken into a stirred-tank adsorber⁹⁾, and while the liquid was being mixed by a turbine impeller at a specified speed, a predetermined amount of hydroxyapatite powder was added. A small amount of the liquid was sampled at appropriate time intervals to measure the concentration change of the solution with time. The amount of apatite powder added (dose) was usually in the range of 0.25 kg/m^3 to 1.0 kg/m^3 .

For binary and ternary component systems, usually nitrates of Pb^{2+} , Cu^{2+} and Cd^{2+} , respectively, were used and the pH of the solution was adjusted to 5.0

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by the addition of nitric acid. The concentrations of each solution were changed considering their molar fractions while keeping total concentration constant. The concentrations of each heavy-metal ion were determined by use of an atomic absorption photometer, Hitachi Model Z-6000.

The temperature of the solutions was maintained usually at 298 K by immersing the tank in a constant-temperature bath. For some runs, the experiments were performed at 308 K and 318 K, respectively.

The hydroxyapatite samples which remained after each run were analyzed to determine their crystallite structures by use of an X-ray diffractometer, Shimadzu Model XD-3A.

2. Results and Discussion

2.1 Single-component adsorption (Removal)

1) Equilibrium relationship, suitable pH range and influence of anion on the process The phenomenon taking place in the tank adsorber is a simple ion exchange between a part of the Ca^{2+} in the apatite structure and divalent heavy-metal ions M^{2+} in the aqueous phase, provided no exchange of Ca^{2+} with H^+ takes place. Therefore, the exchange reaction can be described as follows:

where M^{2+} denotes respective divalent ions.

The mass balance for M^{2+} ions can be expressed as follows.

$$mq = V(C_0 - C) \quad (1)$$

Equation (1) is the so-called operational line, and at infinitely long time, q and C will reach equilibrium with each other. All symbols are summarized in the Nomenclature.

Table 1 shows some results for Pb^{2+} , Cu^{2+} and Cd^{2+} chlorides and nitrates at various pH values. It is found that when the pH of the solution was above 4, the amount of M^{2+} exchanged with Ca^{2+} , expressed in terms of mol/m^3 , was almost the same for each ion. When the pH was smaller than 3, the hydroxyapatite crystals were dissolved gradually by neutralization reaction with H^+ and it seemed that the surface area of hydroxyapatite particles increased. Therefore, experiments were conducted in the region of pH 5–6. The phenomena occurring here were ion-exchanges, and rectangular isotherms, or irreversible isotherms⁷⁾, were obtained for all the systems examined⁹⁾. However, for simplicity, the results will be explained in terms of adsorption. Except in such low pH regions as less than 3, it was found that the ion exchange reaction took place without having a serious effect on

Table 1. Amount adsorbed at equilibrium for single heavy-metal ions ($q^* = \text{const.} = K$)

Metallic salt used	pH 3	pH 4	pH 5
	q^* [mol/kg]	q^* [mol/kg]	q^* [mol/kg]
$\text{Pb}(\text{NO}_3)_2$	6.032	0.579	0.574
$\text{Cu}(\text{NO}_3)_2$	—	0.803	0.787
$\text{Cd}(\text{NO}_3)_2$	—	0.543	0.534

Metallic salt used	pH 3	pH 4	pH 5
	q^* [mol/kg]	q^* [mol/kg]	q^* [mol/kg]
PbCl_2	1.255	0.362	0.338
CuCl_2	—	0.835	0.787
CdCl_2	—	0.516	0.516

the apatite structure.

Regarding the values of equilibrium amount adsorbed q^* of Pb^{2+} , it was found that q^* for $\text{Pb}(\text{NO}_3)_2$ solution at pH 3 was very large compared with that for PbCl_2 solution at the same pH. The reason seemed to be that the hydroxyapatite crystallites structure was destroyed by exchanging Ca^{2+} with H^+ , and then OH^- also existing in the structure was lost by the change with NO_3^- in the solution. However, the OH^- ions in the hydroxyapatite structure did not change with Cl^- so much as with NO_3^- .

Above pH 4, the values of q^* were almost constant for each ion.

2) The rate of exchange of Pb^{2+} with Ca^{2+} ⁴⁾ As the exchange reaction between Pb^{2+} and Ca^{2+} described by Eq. (1) is very fast and seems to take place at the surface of the apatite particles, the following rate equation can be given:

$$dq/dt = K_F a_P (C - C_s) \quad (2)$$

The initial conditions and the equilibrium relation can be written as follows.

$$C = C_0, \quad q = 0 \quad (t = 0) \quad (3)$$

$$q^* = \text{const.} = k \quad (t > 0) \quad (4)$$

$$q = (q^*/C^*)C_s \quad (5)$$

From these equations, one could easily obtain Eq. (6)⁹⁾:

$$\begin{aligned} C/C_0 = 1 - \frac{1}{(1 + C^*V/km)} \\ \times [1 - \exp\{-(1 + C^*V/km)(mK_F a_P/V)t\}] \end{aligned} \quad (6)$$

* $a_P = 6/(\text{particle size})(\text{particle density})\phi_s$; where ϕ_s is the shape factor and is 0.86 for particles of irregular shape.

If the rate-determining step is only liquid-film diffusion, K_F must be the same as the liquid-film mass transfer coefficient, k_F , given by some correlations.^{1,2,5,6)} Using a suitable set of physical properties of the liquid solution, k_F was calculated. **Figure 1** shows a comparison between observed results (points) and decay curves calculated from Eq. (6) for respective conditions.⁹⁾ The values of a_p were determined from the particle size and density of the sample, as they are irregular, assuming the shape factor of the particles to be 0.86. **Table 2** shows $k_F a_p$ calculated from several equations, and **Table 3** shows results obtained from curve-fitting for each ion.

As the experimental results for Pb^{2+} are almost the same as those calculated, it was concluded that Pb^{2+} exchanged very quickly with Ca^{2+} and that the resistance to mass transfer existed only in film diffusion.

From the measurement of $K_F a_p$ for Pb^{2+} - Ca^{2+} for the three temperatures, and plotting the values of $K_F a_p$ against $1/T$, the value of activation energy was obtained as 18.8 kJ/mol. This value again indicates that the process is controlled by film diffusion. The equilibrium amount adsorbed of Pb^{2+} did not change with change in temperature.

3) Rate of exchange of other ions than Pb^{2+} Superposing the measured decay curves with those calculated for various values of $K_F a_p$, one could easily determine the values for respective runs. Table 3 shows some results for Cu^{2+} and Cd^{2+} adsorption.

As can be seen, the values for the above two systems are much smaller than those of $k_F a_p$ calculated.

From the change of $K_F a_p$ with temperature, the values of activation energy were determined to be 27.3 kJ/mol and 32.0 kJ/mol, respectively, for Ca^{2+} and Cd^{2+} adsorption.

Since these values are clearly much larger than those for the case of Pb^{2+} - Ca^{2+} exchange, it seems that the rate process is controlled by processes other than film diffusion. Namely, as the ion radius of Pb^{2+} is the same as that of M1 and M2 sites of Ca^{2+} in the hydroxyapatite structure, and it seems that Pb^{2+} can exchange with both sites without any selection. Consequently, the rate process is controlled by film diffusion. On the other hand, the ion radius of Cu^{2+} is beyond the range of M1 and M2 sites (column site) and the Cu^{2+} ions are hard to exchange with Ca^{2+} . Also, the radius of Cd^{2+} ion is almost the same as that of Ca^{2+} . However, because the electronegativity of Cd^{2+} is smaller than that of Pb^{2+} , Cd^{2+} seems to be difficult to exchange with Ca^{2+} . In addition, hydrated ions of Cu^{2+} and Cd^{2+} in the liquid must be dissociated before exchanging with Ca^{2+} . Therefore, it seems that the process of dehydration is one of the rate-determining steps. Considering these facts, it is reasonable that smaller values of $K_F a_p$ are ob-

Fig. 1. Comparison between calculated concentration-decay curves of Pb^{2+} (nitrate) exchange at pH 4 and experimental results

Table 2. Liquid-film volumetric mass transfer coefficient $k_F a_p \times 10^3$ [$\text{m}^3/\text{kg s}$] obtained from several correlation equations

Equations	$k_F a_p \times 10^3$ [$\text{m}^3/\text{kg s}$]		
	$\text{Pb}(\text{NO}_3)_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{Cd}(\text{NO}_3)_2$
Baker-Treybal ¹⁾	5.45	5.07	5.07
Harriott ²⁾	10.72	9.64	9.61
Leterman ⁵⁾	5.26	4.79	4.78
Levins-Glastonbury ⁶⁾	4.93	4.46	4.45

Equations	$k_F a_p \times 10^3$ [$\text{m}^3/\text{kg s}$]		
	PbCl_2	CuCl_2	CdCl_2
Baker-Treybal	5.53	5.14	4.94
Harriott	10.98	9.64	9.86
Leterman	5.37	4.88	4.87
Levins-Glastonbury	5.04	4.55	4.54

Table 3. Overall volumetric mass transfer coefficient $K_F a_p \times 10^3$ [$\text{m}^3/\text{kg s}$] obtained from curve-fitting (Temp. = 298 K)

Dose	$\text{Pb}(\text{NO}_3)_2$		$\text{Cu}(\text{NO}_3)_2$		$\text{Cd}(\text{NO}_3)_2$	
	pH 4	pH 5	pH 4	pH 5	pH 4	pH 5
$m \times 10^3$ [kg]						
0.2	3.6	—	—	—	—	—
0.5	4.2	4.1	—	—	—	—
1.0	4.2	3.5	0.7	1.0	1.0	0.6
1.5	4.8	—	—	—	—	—
2.0	—	4.5	0.4	0.3	0.7	0.6
4.0	—	—	0.9	0.9	0.8	0.7

Dose	PbCl_2		CuCl_2		CdCl_2	
	pH 4	pH 5	pH 4	pH 5	pH 4	pH 5
$m \times 10^3$ [kg]						
0.5	4.8	4.8	—	—	—	—
1.0	4.9	4.8	0.6	0.5	0.7	0.8
1.5	4.4	—	—	—	—	—
2.0	4.4	3.5	0.5	0.3	0.6	0.6
4.0	—	—	0.6	0.7	0.8	0.8

tained for Cu^{2+} and Cd^{2+} exchange with Ca^{2+} .

2.2 Binary- and ternary-component systems

1) Equilibrium relationship of binary and ternary component systems For binary- and ternary-component systems of the heavy metal ions, the amount adsorbed at equilibrium can be shown by Eq. (7).

$$q_i = (V/m)(C_{0i} - C_i^*) \quad (7)$$

Where i means one of the heavy metal ions in solution.

When the molar fraction of component A for total initial cations is expressed as X_A and that in the solid phase for total amount adsorbed at equilibrium is denoted as Y_A , the following equations can be derived:

$$X_A = C_1^* / \Sigma C_i^* \quad (8)$$

$$Y_A = q_1^* / \Sigma q_i^* \quad (9)$$

In most cases, it is convenient to use subscript A for the most-adsorbable component. By use of the selectivity coefficient based on concentration, K_c , the following relation between X_A and Y_A can be given.

$$Y_A / (1 - Y_A) = K_c \{ X_A / (1 - X_A) \} \quad (10)$$

Figure 2 shows the results for the relation between X_A and Y_A at various ionic ratios, and three total ionic concentrations, C_0 . As can be seen from the figure, K_c is almost constant irrespective of ionic ratio X_A , while K_c , i.e. the relation between X_A and Y_A , changed with the change in total concentration. For the Cu^{2+} - Cd^{2+} system, however, K_c did not change with change in total concentration.

K_c for each system was calculated from the results and the values are listed in **Table 4**.

As to the ternary-component system, results shown in **Fig. 3** were obtained for various total concentrations and the K_c values are shown in **Table 5**. K_c was constant irrespective of ionic concentration.

2) Rate of exchange for binary- and ternary-component systems It seems that ion exchange takes place at the surface of the apatite particles similarly to that for single-component systems, and the following equation can be given:

$$q_i = (q_i^* / C_i^*) C_{si} \quad (11)$$

The rate equation is as follows.

$$dq_i / dt = K_F a_{pi} (C_i - C_{si}) \quad (12)$$

Initial condition is expressed as

$$C = C_0, \quad q = 0 \quad (13)$$

From these equations one can obtain Eqs. (14)–(19).

$$C_i / C_{0i} = 1 - \frac{1}{S_i} [1 - \exp\{-S_i(mK_F a_{pi} / V)t\}] \quad (14)$$

The following equation can be derived.

Fig. 2. Adsorption isotherm for binary system (Pb^{2+} - Cu^{2+})

Table 4. Molar selectivity coefficient K_c for binary systems

Systems	$\bar{C}_0$ [mol/m ³]	K_c [—]
Pb^{2+} - Cu^{2+}	0.5	8.3
	2.5	7.3
	4.5	3.9
Pb^{2+} - Cd^{2+}	0.5	8.0
	2.5	4.8
	4.5	3.6
Cu^{2+} - Cd^{2+}	0.5–4.5	3.5

Fig. 3. Adsorption isotherm for ternary system (Pb^{2+} - Cu^{2+} - Cd^{2+})

Table 5. Molar selectivity coefficient K_c for ternary systems Pb^{2+} - Cu^{2+} - Cd^{2+}

$\bar{C}_0$ [mol/m ³]	K_c [—]
0.5	11.6
1.0	4.2
3.0	3.2

For binary-component systems:

$$S_1 = 1 + C_1^* C_2^* / K_c C_1^* (C_{02} - C_2^*) \quad (15)$$

$$S_2 = 1 + K_c C_1^* C_2^* / C_2^* (C_{01} - C_1^*) \quad (16)$$

For the ternary-component system:

$$S_1 = 1 + \frac{C_1^* (C_2^* + C_3^*)}{K_c C_1^* (C_{02} + C_{03}) - (C_2^* + C_3^*)} \quad (17)$$

$$S_2 = 1 + \frac{K_c C_1^* C_2^*}{(C_{01} - C_1^*) (C_2^* + C_3^*) - K_c C_1^* (C_{03} - C_3^*)} \quad (18)$$

$$S_3 = 1 + \frac{K_c C_1^* C_3^*}{(C_{01} - C_1^*) (C_2^* + C_3^*) - K_c C_1^* (C_{02} - C_2^*)} \quad (19)$$

As to binary-component systems, **Fig. 4** shows an example of a comparison between values of C_i/C_{0i} (points) obtained from experiments and the decay curves calculated from Eqs. (14)–(16) for suitable values of $K_F a_p$. The two results agreed very well for almost all ranges of time, and values of $K_F a_p$ for corresponding conditions were determined.

For the ternary-component system, the experimental values were similar to those calculated from Eqs. (14), (17)–(19). The results are shown in **Fig. 5**. Again $K_F a_p$ was determined.

The values of $K_F a_p$ determined by curve-fitting are listed in **Table 6**. From Tables 5 and 6, it seems that the values $K_F a_p$ for binary- and ternary-component systems are almost the same as those obtained for single-component systems.

2.3 Structure of hydroxyapatite after collecting heavy-metal ions

The difference in the structure of the resulting apatites obtained from the exchange in NO_3^- and Cl^- solutions, respectively, was studied by X-ray diffraction. From results, it was concluded that the apatite structure was maintained in the Cl^- system even at pH as low as 3.0, even though Ca^{2+} -hydroxyapatite was unstable at such low pH. The structure of the apatite formed in the presence of Cl^- seemed to stabilize by the synergic effect of Pb^{2+} and Cl^- ions even at such a low pH as 3.0.

The apatite structure formed in the NO_3^- and Cl^- system was maintained without the influence of H^+ at pH 4.0 is probably due to the rather short contact time.

For the structures of apatite formed in binary- and ternary-component systems, Cu^{2+} and Cd^{2+} peaks were not so clear as that for Pb^{2+} because of the smaller amounts uptaken. In any case, the hydroxyapatite structure was maintained and the divalent heavy metal ions were held in the structure.

2.4 On the feasibility of hydroxyapatite for heavy metal ions removal

As the removal of divalent heavy metal ions can be

Fig. 4. Experimental plots and calculated curves of Eqs. (14), (15) and (16) for binary system (Pb^{2+} - Cu^{2+})

Fig. 5. Experimental plots and calculated curves of Eqs. (14), (17), (18) and (19) for ternary system

Table 6. Overall volumetric mass transfer coefficient $K_F a_p \times 10^3$ [$\text{m}^3/\text{kg s}$] obtained from curve-fitting for the binary and ternary system Pb^{2+} - Cu^{2+} :

$\bar{C}_0$ [mol/m ³]	$K_F a_{p1} \times 10^3$ [m ³ /kg s]	$K_F a_{p2} \times 10^3$ [m ³ /kg s]
0.49	4.5	0.8
2.40	2.5	0.1
4.57	4.0	0.5

Pb^{2+} - Cu^{2+} - Cd^{2+} :

$\bar{C}_0$ [mol/m ³]	$K_F a_{p1}$	$K_F a_{p2}$ $\times 10^3$ [m ³ /kg s]	$K_F a_{p3}$
0.45	5.5	0.5	0.2
1.00	5.0	0.5	0.2
3.02	2.0	0.3	0.2

carried out with the addition of hydroxyapatite powder with rather high removal capacity and the resulting powder can be easily separated from the water, this process will be useful if the cost is low enough. For Pb^{2+} removal in particular, this process will be very effective.

Conclusion

Batch-wise adsorption experiments were performed to obtain equilibria and rate data for the removal of Pb^{2+} , Cu^{2+} and Cd^{2+} ions (single, binary, and ternary ions, respectively) from aqueous solutions by the addition of hydroxyapatite powder. As for single-component adsorption equilibria, the processes were ion exchanges (irreversible), and their isotherms were rectangular. Binary and ternary data were expressed in terms of selectivity coefficient. Values of mass transfer coefficient were determined from analyses of concentration decay curves. Pb^{2+} was uptaken very quickly, while the other two ions showed some resistances other than film diffusion.

Since the heavy metal ions uptaken can be held in the apatite structure, the use of this process will be feasible provided that apatite powder is supplied at a low price.

Acknowledgement

The authors would like to express their deepest thanks to Prof. T. Suzuki of Yamanashi University for his advice in performing this study. They also thank T. Ito and Y. Ohkawa for their assistance in experimental works. The study was partly supported by a Grant in Aid for Scientific Research (No. 61430023) by the Ministry of Education, Science and Culture.

Nomenclature

a_p	= surface area of particles	$[\text{m}^2/\text{kg}]$
C	= concentration in liquid phase	$[\text{mol}/\text{m}^3]$
C_0	= initial concentration	$[\text{mol}/\text{m}^3]$
C^*	= equilibrium concentration	$[\text{mol}/\text{m}^3]$
C_s	= concentration at particle-liquid interphase	$[\text{mol}/\text{m}^3]$
$\bar{C}_0$	= total initial concentration	$[\text{mol}/\text{m}^3]$
K_c	= molar selectivity coefficient based on concentration	[—]

$k_F a_p$	= liquid-film volumetric mass transfer coefficient	$[\text{m}^3/\text{kg s}]$
$K_F a_p$	= overall volumetric mass transfer coefficient	$[\text{m}^3/\text{kg s}]$
m	= mass of adsorbent	$[\text{kg}]$
q	= amount adsorbed	$[\text{mol}/\text{kg}]$
q^*	= amount adsorbed at equilibrium	$[\text{mol}/\text{kg}]$
S_i	= parameters defined by Eqs. (14)–(19)	[—]
t	= time elapsed	$[\text{s}]$
V	= volume of liquid	$[\text{m}^3]$
X_A	= molar fraction of key component for total initial component	[—]
Y_A	= molar fraction of key component for total amount adsorbed at equilibrium	[—]

<Subscripts>

A	= most adsorbable component of binary or ternary system
F	= fluid
i	= component
0	= initial
$1, 2, 3$	= components in the order of adsorbability
s	= solid-liquid interphase

Literature Cited

- 1) Baker, J. J. and R. E. Treybal: *AIChE J.*, **6**, 289 (1960).
- 2) Harriott, P.: *AIChE J.*, **8**, 93 (1962).
- 3) "Kagaku-Kougaku-benran (4th Ed.)," p. 847, Maruzen, Tokyo (1978).
- 4) "Kagaku-Kougaku-benran (5th Ed.)," p. 1315, Maruzen, Tokyo (1988).
- 5) Leterman, R. D., J. E. Quon and R. S. Gemmell: *JWPCF*, **46**, 2536 (1974).
- 6) Levins, D. M. and J. R. Glastonbury: *Trans. Inst. Chem. Engrs.*, **50**, 132 (1972).
- 7) Suzuki, M. and K. Kawazoe: *J. Chem. Eng. Japan*, **5**, 346 (1974).
- 8) Suzuki, T., T. Hatsushika and M. Miyake: *J. Chem. Soc., Faraday Trans.*, **1**, **78**, 3605 (1983).
- 9) Takeuchi, Y., T. Suzuki and H. Arai: *J. Chem. Eng. Japan*, **21**, 98 (1988).