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The Cementation of Cadmium Ion in Aqueous Solution by a Zinc Column Test

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ABSTRACT

A series of column experiments on the cementation of cadmium ions by zinc powder were conducted as a function of amount of zinc dosage, the initial concentration of cadmium ion, flow rates, depth of bed, and the addition of surfactant to obtain more applicable design data. Cementation of cadmium by the zinc column test was shown to be a feasible treatment process to achieve a high degree of cadmium removal within a fairly reasonable contact time. The efficiency of utilization of a zinc powder bed improved with increasing empty bed contact time (EBCT), but the cementation capacity of zinc powder usually increased with decreasing EBCT value. The breakthrough curve was extended and the effective cementation capacity of the zinc cementation column was raised by adding

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small quantities of sodium dodcyl sulfonate (SDS) surfactant, probably due to the morphological change involving the cemented cadmium deposits on the zinc surface. Three different adsorption models, the bed-depth-service-time (BDST) model, the Wolborska model, and the Clark model are used to simulate the experimental data. The cementation behavior of cadmium ions in a zinc powder column can be well described by the BDST model, but the fitted rate constant of cementation (k_{ads}) decreased with increasing EBCT, thus, it is necessary to modify the BDST model to further estimate the exhaust time of the zinc powder column under various conditions. The fitted results of the other two models indicate higher deviations to the experimental results possibly because the cementation rate was mainly determined by the surface reaction step.

Key Words: Cementation; Cadmium ions; Zinc powder column; BDST model.

INTRODUCTION

Cadmium species can be present in a variety of forms in wastes or in the environment. Even though some forms are insoluble in water, cadmium is supposed to be relatively mobile in the aquatic environment. Cadmium is a known animal teratogen and reproductive toxin. Cadmium is carcinogenic in animals exposed by inhalation and may also be in humans. It has chronic effects on the kidneys, and background levels of human exposure are thought to provide only a relatively small margin of safety for these effects.[1] Growing concerns on the removal of cadmium from the aquatic environment has been a subject of increasing importance. Currently, the most frequently practiced treatment technology for the removal of heavy metals from aqueous solutions is chemical precipitation, which merely relocates the heavy metals from aqueous phase to solid phase, leave further sludge problems to be solved. Therefore, the removal of heavy metals from numerous industrial wastewaters has stimulated vigorous research activities in the development of a number of specialized treatment technologies with the possibility of metal recovery.

The cementation process has been demonstrated to be a feasible alternative because of its relative simplicity, ease of control, and the possible recovery of valuable metals. Theoretically, the removal of heavy metals from aqueous solutions by the cementation process is capable of reducing these soluble metal species from aqueous solutions almost completely into solid form, if the cementation reaction is taken long enough. However, the sufficiency of redox potential and excessive consumption of sacrificing metals limits the application of this process.

The cementation process is a common practice for metallurgical industries and is a spontaneous redox reaction utilizing a less expensive and electropositive sacrificing solid metal for the recovery of another more expensive and electronegative dissolved metal species originally presented in the aqueous solutions. For applications in wastewater treatment, cementation processes are usually employed for the deposition of a more toxic metal reduced by a less toxic metal. For instance, the removal of cadmium ions by zinc cementation studied in this research is achieved spontaneously because the redox potentials of zinc and cadmium are 0.76 V and 0.315 V, respectively, and can be expressed by the following redox equation:

$$Zn + Cd^{2+} = Zn^{2+} + Cd \tag{1}$$

Compared to the cation exchange resin method, a major advantage of such a reduction by cementation is that noble metals (such as cadmium) are obtained in an easily recoverable metallic form in a simple one-step process. Although lots of experimental studies have been conducted successfully for the removal of various heavy metals from wastewaters by the cementation process,[1–5] previous study on the removal behaviors of heavy metals by cementation in a column test is rare compared to it in suspension systems. Furthermore, the results reported by several researchers[6–9] indicate that the effect of surfactant on the cementation rate and the morphology of cemented metal deposits were highly dependent on the experimental conditions and some controversial findings were reported about the effect.

In this study, a series up-flow column cementation experiments was performed to examine factors governing the cementation behaviors of cadmium ions on zinc powder surface. The primary interest is to investigate the effect of operating factors, such as dosage of zinc, flow rate, initial concentration of Cd^{2+}, and the addition of SDS surfactant on the cadmium removal by cementation in aqueous solutions. The temporal behaviors of cementation are examined, and the determined reaction rates and kinetic parameters obtained from experimental data are expressed and discussed by the BDST model.

MATERIALS AND METHODS

Materials

Zinc powder (from Merck, Inc., Whitehouse station, NJ, USA) of greater than 99.99% purity with mean sizes of 45 μm was used as the sacrificing metal for cadmium removal without any screening process in this research. The chemicals used in this study certified reagent grade chemicals and all experimental solutions were prepared with double distilled water. Standard cadmium sulfate ($3CdSO_4(8H_2O$ with a molecular weight of 769.5 g/mole) solutions of 1000 mg/L (from Merck) were diluted to prepare required cadmium solutions with different concentrations. Standard acid and base solutions (NaOH and H_2SO_4) were prepared weekly for pH adjustment.

General Procedures

A schematic diagram of the experimental apparatus is shown in Fig. 1. The up-flow column adsorption experiments were performed for all kinetic studies. The laboratory apparatus of up-flow column test consisted of vertical fixed-bed columns, with an inner diameter of 3 cm, 10 cm height, and up to two columns that could be operated simultaneously. Due to the small size of zinc powder, the phenomenon of channeling would occur if the column was only filled with zinc powder. Thus, each column was charged with predetermined quantities of zinc powder mixed with appropriate amounts of small glass bead with 1-mm diameter in the column. The glass bead needs to be prewashed with 1-N H_2SO_4 solutions to avoid the adsorption of cadmium

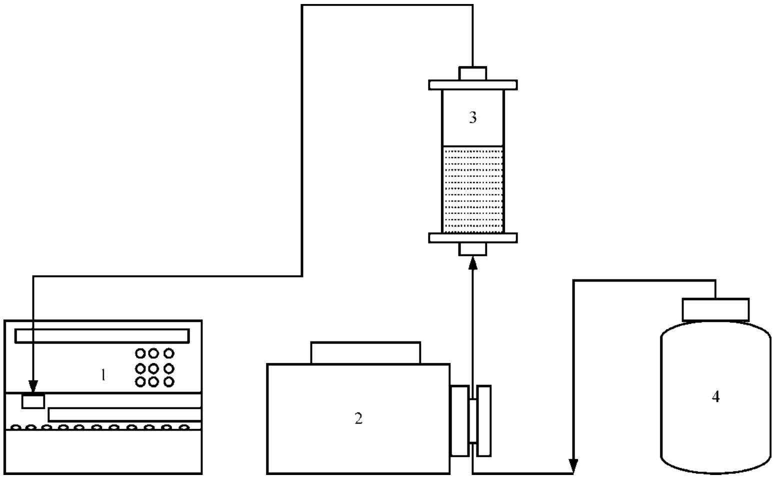

Figure 1. The experimental apparatus. (1) Fractional collector, (2) micro-pump, (3) zinc column, and (4) vessel with the cadmium-containing solution.

onto the glass bead, which was confirmed by the blank test. After appropriate mixing, the distribution of zinc powder within the glass bead was assumed to be uniform in the chemisorption process. A 5-L vessel filled with the cadmium-containing solution of desired concentration was to be the source of wastewaters. The solution pH of all the experiments was adjusted and maintained at pH 4 during the reaction course by adding 1-N NaOH and 1-N H_2SO_4 solutions. At this pH level, the major cadmium specie is free cadmium ions by the speciation calculation with a typical pe-pH relationship based on the Nernst equation. The zinc powder is oxidized by the dissolved oxygen in an oxygen-rich aqueous environment, thus the mass calculation of reacting species will be mistaken. To avoid the possible effects caused by the presence of dissolved oxygen in aqueous solutions, the experimental work of this research was carried out under a nitrogen atmosphere and the dissolved oxygen levels were kept under 0.5 mg/L and was monitored by an Orion 820 dissolved oxygen meter throughout the course of the reaction. Thus, the only significant side redox reaction for cadmium cementation by zinc is assumed to be the reaction between zinc and hydrogen ions. In this study, four zinc dosages of 0.15, 0.2, 0.3, and 0.4 g were charged. Feed solution also could be divided into two channels and maintained at constant flow rate with a masterflux pump to feed into the columns. Four flow rates of 300, 400, 500, and 600 mL/hr were used. The space time was varied with different flow rate. The temperature of solution was maintained at $25.0 \pm 0.2°C$ by a water jacket in all of the experiments. A portion of the reacted solution was sampled at certain reaction time periods and then filtered using a 0.45-μm filter. The cadmium concentrations were analyzed by a GBC 904AA atomic adsorption spectrophotometer. If necessary, the concentrations of surfactant and chelating agent were determined by an OIC 700 TOC analyzer.

Description of the Models

Because the reaction characteristics of cementation is comparable to a heterogeneous adsorption process,[10] three different adsorption models: the bed-depth-service-time (BDST) model, Wolborska model, and Clark model are used to describe the cementation behaviors of cadmium species from the zinc column in this work. In a heterogeneous adsorption process, four steps are considered to have occurred before adsorbates can attach to an adsorbent surface[11]: (1) mass transfer from the bulk phase to the surface of the particle, (2) adsorption on external adsorbent surface sites, (3) diffusion in the pore/surface, and (4) adsorption at internal surface sites. Therefore, adsorption of metals onto porous media (in this case, it means zinc powder with porous cadmium deposits) can be either a diffusion (including both film transfer and pore/surface diffusion resistances) or surface reaction- (combining both external and internal surface reaction resistances) control mechanisms. However, because there are no exact rules to determine the appropriate mechanism for a specific adsorption process, testing and/or fitting procedures are usually used to identify the best system model. The briefs of the above models are as introduced as follows.

BDST Model

Some popular models assume that there is no film transfer resistance or pore and/or surface diffusion resistance for metal transport from the bulk solution to adsorbent surface. Bohart and Adams[12] assumed that the rate of adsorption was mainly determined by the surface adsorption on the adsorbent surface sites and proportional to the concentrations of adsorbed species and the surface adsorption sites based on the assumptions including no diffusion limitation, uniform surface site energy, and monolayer adsorption were made. The bed-depth-service-time (BDST) model[13] is a modified form of the theory of Bohart and Adams that relates the service time of a column to the height of adsorbent in the bed. Owing to the fact that the bed mass is directly proportional to the bed height for an adsorption column of fixed diameter, the bed mass was used instead of the bed height in the BDST model, as shown in the following equation:

$$t = \frac{q_0}{C_0 v} M - \frac{1}{k_{ads} C_0} \ln\left(\frac{C_0}{C_A} - 1\right) \tag{2}$$

where t is the service time (min), q_o is the adsorption capacity (mmole/g), C_0 is the initial concentration of pollutants (mM), k_{ads} is the second order adsorption rate constant (L/min-mole), C_A is the effluent concentration of pollutants at t time (mM), v is the constant flow rate of the stream (mL/min), and M is the dosage of absorbent (g).

The k and q_o values are calculated by fitting the BDST equation to the experimental adsorption data. Once k and q_o values are determined from column tests, the adsorption data for other flow rates or zinc dosages can be modeled by the BDST equation.

Wolborska Model

The second simplified adsorption model was derived by Wolborska.[14] In this model, the adsorption rate was suggested to determine by the outer mass-transfer step. This model is applicable to an adsorption system with low concentration of pollutants and can be illustrated by:

$$\ln \frac{C_A}{C_0} = \frac{k_m C_0}{N_0} t - \frac{k_m D}{v} h \tag{3}$$

where h is the distance from the column entrance (cm), D is the axial diffusivity coefficient of pollutants (cm^2/min), k_m is the outer mass transfer coefficient of pollutants (min^{-1}), and N_0 is the total amount of adsorption capacity (mM).

Clark Model

The Clark model is derived from the combination of the mass transfer concept and Freundlich isothermal adsorption model by Clark[15] and can be shown as:

$$\frac{C_A}{C_0} = \frac{1}{(1 + Ae^{-\theta t})^{1/n-1}} \tag{4}$$

where

$$A = \left(\frac{C_0^{n-1}}{C_A^{n-1}} - 1 \right) e^{\theta t} \tag{5}$$

$$\theta = \frac{\mathrm{K_m}}{\mathrm{G_s}} \mathrm{v_m}(\mathrm{n} - 1) \tag{6}$$

$$\mathrm{v_m} = \frac{\mathrm{vC_0}}{\mathrm{N_0 + C_0}} \tag{7}$$

and G_s is the flow rate per cross area ($\mathrm{m}^3/\mathrm{h} - \mathrm{m}^2$), A_c is the cross area of column (m^2), K_m is the mass-transfer coefficient of pollutants (h^{-1}), v_m is the velocity of stream (cm/min), and K_e, are the n is the equilibrium constants.

In this model, the adsorption rate was also recommended to determine by the outer mass-transfer step.

RESULTS AND DISCUSSION

The cementation behaviors of cadmium ions in the stream was examined under various zinc dosages, flow rates, influent concentrations of cadmium ions, and the addition of SDS surfactant to investigate the removal efficiency of the metal pollutant by using the zinc column.

Effect of Zinc Dosage

To assess the removal efficiency of cadmium ions by the cementation column, the terms of $t_{0.5}$ and EBCT were adopted. The $t_{0.5}$ is defined as the life of carbon bed to be operated to reach a 50% breakthrough concentration. The empty bed contact time (EBCT), which is directly proportional to bed depth or inversely proportional to flow rate, is an important factor to affect the value of $t_{0.5}$. The cementation rates of cadmium ions at various zinc dosage are shown in Fig. 2 and the corresponding $t_{0.5}$ and EBCT values of the breakthrough curves are shown in Table 1. The breakthrough curves present in a similar shape in all cases; an initial rapid increase in the residual followed by an abrupt change in the shape before slowly reaching column exhaustion (residual = 100%). It was observed that decreasing zinc dosage accelerated the breakthrough of cadmium through the zinc bed mainly because of the shortage of the amount of zinc to cement cadmium. Adding the double amount of zinc powder (from 0.2 g to 0.4 g), the breakthrough time, which is defined as the time when the effluent Cd^{2+} concentration reaches the influent concentration, was found to extend from 400 minutes to 700 minutes. The relationship between $t_{0.5}$ and zinc dosage was correlated by the power law and can be shown as $t_{0.5} = 2.626\ (\text{zincdosage})^{0.706}$.

Table 1 also shows that the adsorption capacity (q_o) and adsorption rate constant (k_{ads}) calculated by the BDST model decreased with the increasing zinc dosage. It was possibly because that the relative bulk porosity in zinc bed was diminished when the amount of zinc dosage increased to reduce the cementation efficiency.

Figure 3 illustrates the temporal distributions of cadmium ions and the dissolved zinc ions in the effluent during the cementation course at zinc dosage of 0.2 g and pH 4. The residual concentrations of zinc were found to be almost equal to the stoichiometric consumption by cadmium cementation, indicating the side reactions in the $Zn-Cd^{2+}$ cementation system almost did not occur at this reaction condition. The concentration of Zn^{2+} ions in the effluents was quite high ($[Zn^{2+}] = 100\,mg/L$) at $t_{0.5}$ (130 minutes) and may be recovered with appropriate end treatments to avoid secondary pollutions.

Effect of Flow Rate

The flow rate effect on the cementation rates of cadmium ions is shown in Fig. 4 and the corresponding $t_{0.5}$ and EBCT values of the breakthrough curves are shown in Table 2. Increasing the flow rate speeded up the breakthrough of cadmium ions through the zinc bed because of the shorter contact time of

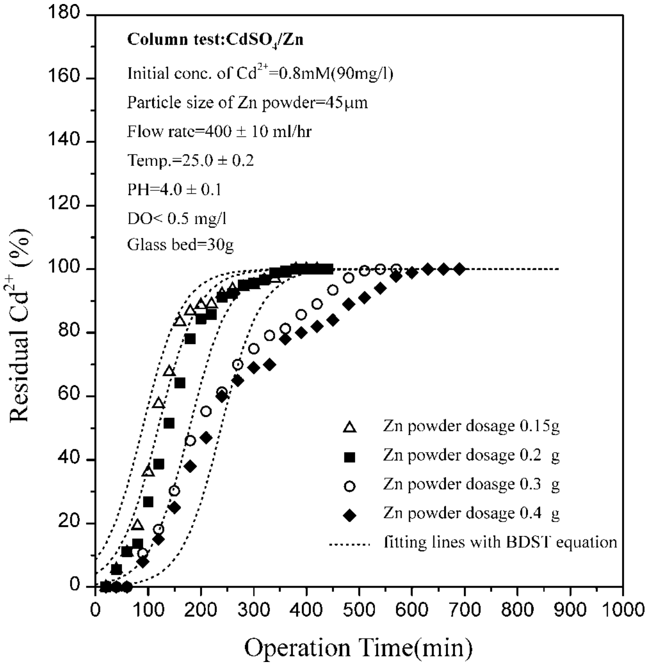

Figure 2. Experimental data and predicted simulations for the results of the effect of zinc dosage on the cementation rates of cadmium ions.

cadmium ions on zinc powder. The breakthrough point was found to be at around the operation time of 250 minutes when the flow rates were larger than 400 mL/hr. When the flow rate was kept at 300 mL/hr, the breakthrough point lengthened to 700 minutes. A power law correlation, $t_{0.5} = 1.912[\mathrm{EBCT}]^{1.177}$,

Table 1. Values of the calculated parameter of the breakthrough curves in Fig. 2.

Zinc dosage (g)	Flow rate (mL/hr)	EBCT (min)	$t_{0.5}$ (min)	k_{ads} (l/min-mmol)	q_o (mmole/g)
0.15	400	1.47	110	0.0407	4.187
0.2	400	1.47	135	0.0311	3.853
0.3	400	1.47	190	0.0175	3.712
0.4	400	1.47	215	0.0147	3.216

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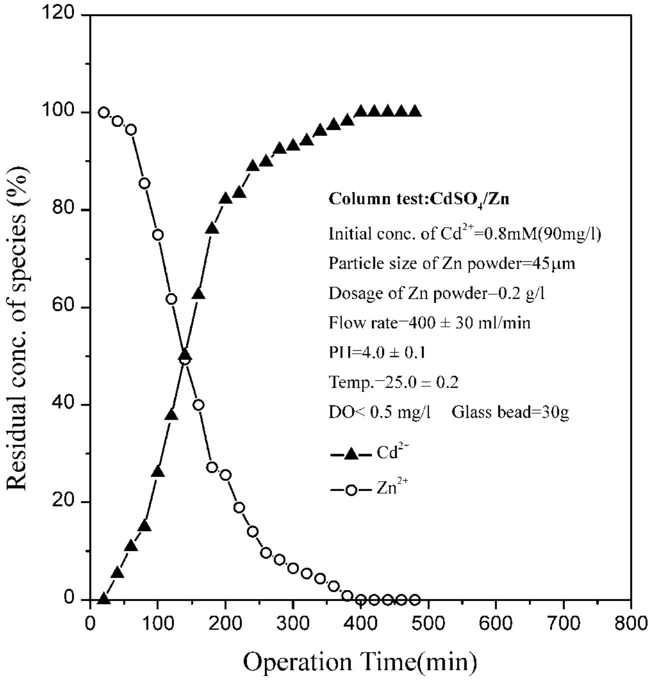

Figure 3. The temporal distributions of cadmium ions and the dissolved zinc ions in the effluent during the cementation course.

for the relationship between $t_{0.5}$ (minute) and EBCT (minute) was obtained, as shown in Fig. 4. An increase in EBCT increased the efficiency of utilization of the zinc bed. The n value was found to be greater than unity and indicates a positive correlation between $t_{0.5}$ and EBCT. Table 2 reveals that the adsorption capacity (q_o) slightly decreased with the increasing flow rate, possibly because the utilization of active sites on zinc surfaces decreased with increasing flow rates. The fitted rate constant of cadmium cementation (k_{ads}) increased with decreasing EBCT, thus, it is necessary to modify the BDST model to further estimate the exhaust time of the zinc powder column under various conditions.

Effect of Initial Concentration of Cd^{2+}

Figure 5 demonstrates the cementation rates of Cd^{2+} at various initial concentrations (80, 100, 170, and 200 mg/L) of cadmium ions at zinc dosage

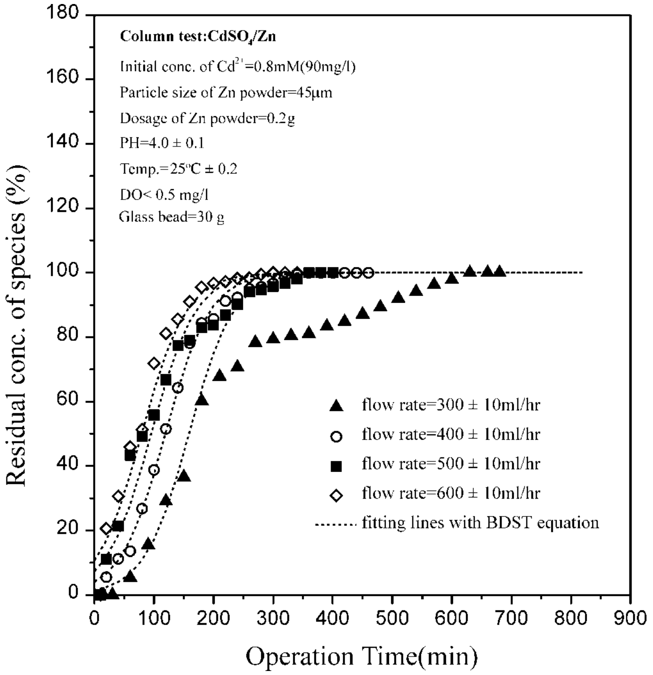

Figure 4. Experimental data and predicted simulations for the results of the effect of flow rate on the cementation rates of cadmium ions.

of 0.2 g and pH 4. It was seen that increasing the initial concentration of cadmium ions quickened the breakthrough of cadmium from the zinc bed because of the amount of the zinc powder was relatively lacking at the higher initial concentration level of cadmium ions. Thus, the breakthrough point

Table 2. Values of the calculated parameter of the breakthrough curves in Fig. 4.

Zinc dosage (g)	Flow rate (mL/hr)	EBCT (min)	$t_{0.5}$ (min)	k_{ads} (l/min-mmol)	q_o (mmole/g)
0.2	300	1.96	170	0.0166	3.781
0.2	400	1.47	140	0.0263	3.799
0.2	500	1.18	90	0.0311	3.087
0.2	600	0.98	80	0.0376	2.905

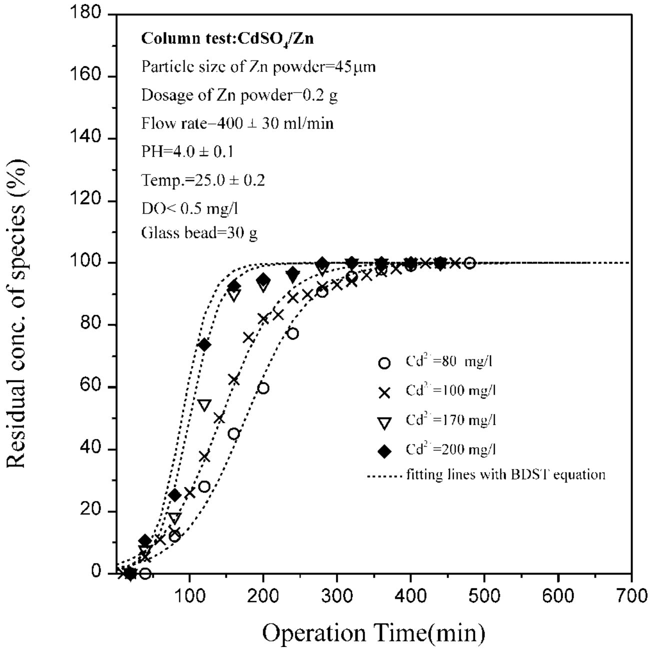

Figure 5. Experimental data and predicted simulations for the results of the effect of initial concentration of Cd^{2+} on the cementation rates of cadmium ions.

among each run was found to be different, as shown in Fig. 5. The values of q_o were found to be slightly increased with increasing the initial concentration of cadmium ions (as shown in Table 3), possibly due to the concentration gradient as well as the driving force of mass transfer of the reactant, being raised by increasing the initial concentration.

Table 3. Values of the calculated BDST parameter of the breakthrough curves in Fig. 5.

Initial concentration of Cd^{2+} (mM)	80	100	170	200
k_{ads} (l/min-mole)	0.0265	0.0311	0.0276	0.0274
q_0 (mmole/g)	3.7993	4.1938	4.2549	4.3548

Effect of Surfactant

The cementation rates of Cd^{2+} at various additional dosages (0, 10, and 20 μM) of sodium dodcyl sulfonate (SDS) at a zinc dosage of 0.2 g and pH 4 is shown in Fig. 6. It was observed that the breakthrough of cadmium from the zinc bed was extended for the operation time of the early 3 hours at SDS dosage of 20 μM compared to that without SDS addition. The SDS is a surface active agent, which will also adsorb on the surface of the zinc and may increase the active sites for adsorption. The later phase of the breakthrough curve at the highest dosage of SDS, which is fast, could be attributed to the degradation of the SDS. The value of the adsorption capacity (q_o) of the run at 20 μM SDS was calculated to be 4.3 mmole/g, which was found to be larger than that of the run without SDS addition (3.8 mmole/g). It is postulated that the addition of SDS into the solutions causes aggregation of cadmium deposits to enlarge the deposit porosity on zinc surface, thus the adsorption capacity of cadmium was lift up according to the morphology study of cemented metal

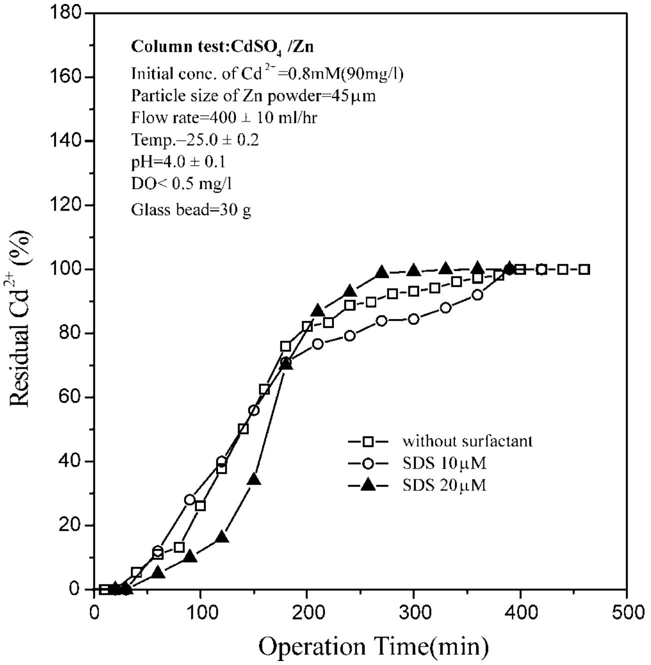

Figure 6. The cementation rates of Cd^{2+} of the runs at various dosages of sodium dodcyl sulfonate (SDS) at zinc dosage of 0.2 g and pH 4.

deposits in our previous work.[16] The later phase of the breakthrough curve of the run at 20 μM SDS was found to quicken faster than the runs of 0 μM and 10 μM SDS. This is because 95% of the cadmium ions has been cemented in the early phase (the first 100 minutes) of the run at 20 μM SDS and the quantity of the active sites on the zinc powder surface was, apparently, lessened in the later phase.

Effect of the Bed Depth

Adding the same zinc dosage of 0.2 g, the cementation rates of Cd^{2+} in the zinc columns charged with the quantities of 20, 30, 40, and 50 g bead, respectively is shown in Fig. 7. The zinc powder and glass beads were mechanically shaken and mixed in a 250-mL container for 2 minutes. The distribution of the zinc powder within glass beads was assumed to be uniform. Increasing the amount of bead added as well as the bed depth extended

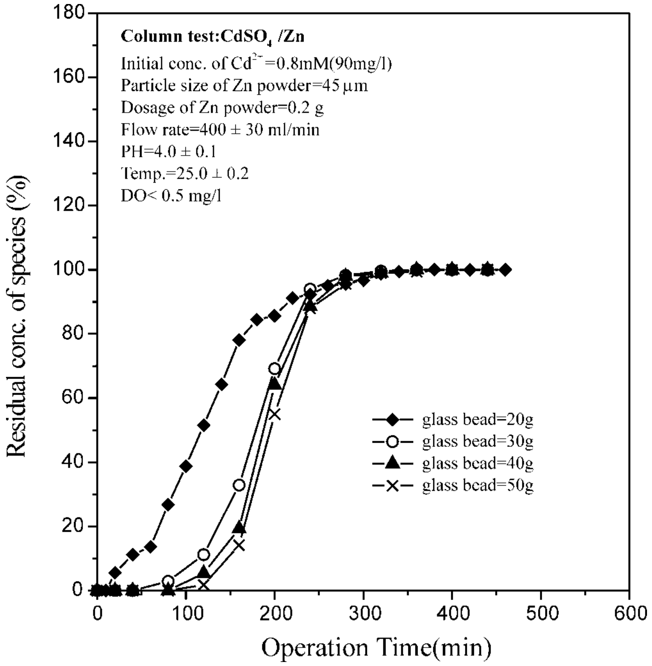

Figure 7. The cementation rates of Cd^{2+} of the runs at various quantities of glass bead charged at zinc dosage of 0.2 g and pH 4.

Table 4. Values of the calculated BDST parameter of the breakthrough curves in Fig. 7.

Quantity of glass bead (g)	20	30	40	50
k_{ads} (l/min-mole)	0.0335	0.0482	0.0567	0.0591
q_0 (mmole/g)	3.1754	4.7432	5.0430	5.2438

the breakthrough of cadmium ions from the zinc bed due to increasing the uniformity of the zinc distribution in the bed. The effective active sites on zinc surfaces increased with increasing the quantity of bead charged at the same dosage of zinc addition. The breakthrough point of the runs with various quantities of bead was found to be at roughly 300 minutes, indicating that the operation life of the zinc cementation column is not influenced by the effect of bed depth. The values of q_o and k_{ads} were found to increase with the increasing the bed depth (Table 4) because of the same reasons just described.

Column Modeling

Bed-Depth-Service-Time (BDST) Model

Effect of Flow Rate

In this research, the k_{ads} and q_o were chosen as fixed values of 0.0335 L/mole-min and 3.799 mmole/g, which was based on the fitted values by using BDST equation of the experimental results with zinc dosage of 0.2 g, and medium flow rate of 400 mL/hr at pH 4, to simulate the breakthrough behaviors of cadmium ions at different flow rates. The comparison with experimental data and predicted simulations, modeled by using the determined q_o and k values at different flow rates, is shown in Fig. 4. It was found that the modeling results can well describe the kinetic behaviors of Cd^{2+} ions at medium and high flow rates in a zinc powder column, but the obvious deviation of the fitting results was found for the later phase at the flow rate of 300 mL/hr. The reason for divergence can be postulated that the porous cadmium deposits aggregated gradually onto the zinc surface during the reaction to make up inner mass-transfer barriers, especially for the later phase of the low flow rate runs. However, the diffusion effect of the reactant is not considered in the BDST model. Based on this inference, it is rational to explain that the k_{ads} values decreased with the decreasing flow rate or with the increasing EBCT (see Table 2).

Effect of Zinc Dosage

Using a similar simulating approach as that of the flow rate effect, the experimental data and predicted results modeled by using the same determined q_o and k values at different zinc dosages is shown in Fig. 2, where noticeable deviation was found. Another approach tried was to only fix q_o to be 3.799 mmole/g, and keep k_{ads} variable. By using the new sets of parameters, the experimental results were much better fitted than the original and are shown in Fig. 8. It was shown that the k_{ads} values usually decreased with the increasing zinc dosage values (see Table 1), indicating that k_{ads} is not an intrinsic value in this research.

Effect of Initial Concentration of Cd^{2+}

Experimental data and predicted simulations modeled by using the determined k_{ads} and q_o chosen as fixed values of 0.0311 L/mole-min and

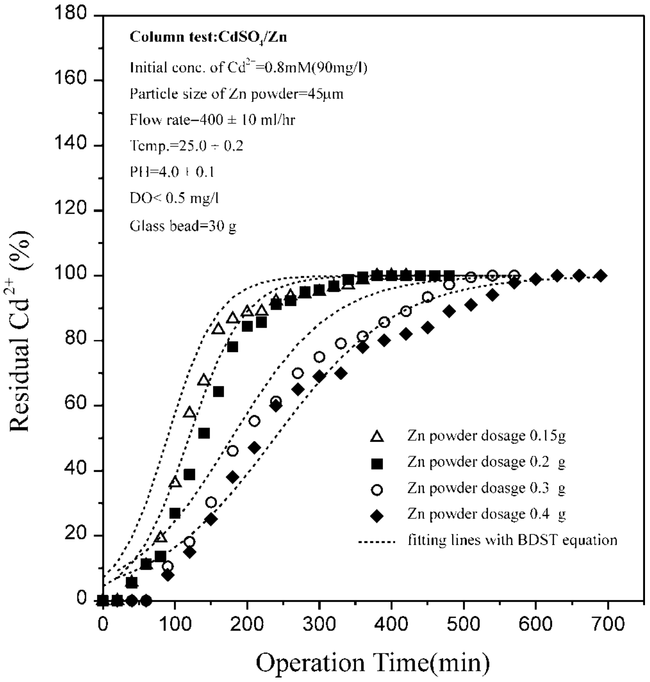

Figure 8. Experimental data and predicted simulations for the results of the effect of zinc dosage on the cementation rates of cadmium ions, where q_o is fixed to be 3.799 mmole/g, and keep k_{ads} to be variable.

3.799 mmole/g for the runs at different initial concentration of cadmium ions is shown in Fig. 5. Fairly good modeled results were found, except those of the runs at higher concentration levels. It was proposed that the basic assumption of the monolayer adsorption in the BDST model was no more suitable for the situation that appeared at heavy deposits (multilayers) on zinc surface, especially at high Cd^{2+} concentration levels. Table 5 presents the difference of the experimental amount and the predicted (maximum) amount of total Cd^{2+} adsorption (cementation) by using the BDST model. It was observed that the relative deviation (D) was between the range of 30% ~ 35%, where the predicted amount of total Cd^{2+} adsorption was determined to be 222.93 mM. The relatively good agreement of fitted results of the breakthrough curves, as shown previously, and the smaller relative deviations of the total amount of Cd^{2+} adsorption, indicate that the cementation rate can be determined by the surface reaction step as the fundamental supposition of the BDST model.

Wolborska Model

The difference between the experimental amount and the predicted amount of total Cd^{2+} adsorption (cementation) by using the Wolborska model [Eq. (3)] is presented in Table 5. It is observed that the relative deviation ranges from 35% to 50%, which is larger than that of the BDST model. The simulation results of the Cd^{2+} breakthrough by this model were found to be relatively inadequate because of the basic assumption in this model that the adsorption rate was determined by the outer mass-transfer step is invalid in the condition of intense deposits on zinc surface. In this situation, the influence of inner mass transfer will be gradually significant on the adsorption rate, thus the discrepancy between the experimental amount and the predicted amount of total Cd^{2+} increased. Furthermore, the fitted results of this model indicate higher deviations in the experimental results, possibly because the cementation rate can be determined by the surface reaction step.

Clark Model

Three major assumptions in the Clark model are: (1) the effluent concentration of pollutants is zero, (2) the adsorption behaviors of pollutants should follow the Freundlich isothermal adsorption model, and (3) the adsorption rate was determined by the outer mass-transfer step. The variation of the experimental amount and the predicted amount of total Cd^{2+} adsorption (cementation) by using the Clark model is also in Table 5. The largest

Table 5. Summary of the differences of the experimental amount and the predicted amount of total Cd^{2+} adsorption (cementation) by using the three models [$N_{o,\ p}$(predicted) = 222.93(mM)].

Factor	Level	K (L/min)[a]	$N_{o,e}$ (mM)[b]	Relative deviation, D (%)[c]	R^2
BDST model					
Flow rate (mL/hr)	300	0.0166	142.67	36.00	0.982
	400	0.0311	143.27	35.73	0.985
	500	0.0263	154.02	30.91	0.978
	600	0.0376	152.68	31.51	0.978
Zinc dosage (g)	0.15	0.0407	155.62	30.19	0.987
	0.2	0.0311	143.27	35.73	0.985
	0.3	0.0175	144.36	35.24	0.986
	0.4	0.0147	147.16	34.06	0.991
Initial concentration of Cd^{2+} (mg/L)	80	0.0265	156.02	30.01	0.982
	100	0.0311	143.27	35.73	0.985
	170	0.0276	160.97	27.79	0.990
	200	0.0274	157.81	29.21	0.984
Wolborska model					
Flow rate (mL/hr)	300	3.73	139.63	37.63	0.921
	400	3.63	128.45	42.23	0.935
	500	2.26	121.18	45.64	0.927
	600	1.75	117.58	47.26	0.918
Zinc dosage (g)	0.15	3.78	132.18	40.71	0.907
	0.2	3.75	124.34	44.36	0.925
	0.3	3.63	137.63	38.26	0.956
	0.4	2.27	139.78	37.43	0.931
Initial concentration of Cd^{2+} (mg/L)	80	2.64	144.19	35.32	0.952
	100	3.75	146.34	34.36	0.945
	170	3.58	140.23	37.43	0.920
	200	3.07	135.92	39.28	0.934
Clark model					
Flow rate (mL/hr)	300	—	75.64	65.99	0.892
	400	—	38.15	82.89	0.825
	500	—	45.94	79.39	0.866
	600	—	32.58	85.39	0.783
Zinc dosage (g)	0.15	—	31.28	85.97	0.792
	0.2	—	38.15	82.89	0.863
	0.3	—	71.58	67.89	0.874
	0.4	—	84.76	61.98	0.810

Table 5. Continued.

Factor	Level	K (L/min)[a]	$N_{o,e}$ (mM)[b]	Relative deviation, D (%)[c]	R^2
Initial concentration of Cd^{2+} (mg/L)	80	—	43.95	80.29	0.788
	100	—	45.68	79.52	0.843
	170	—	46.09	79.33	0.865
	200	—	48.23	78.37	0.843

[a] K = first-order mass-transfer coefficient (L/min).

[b] $N_{o,e}$ = the experimental amount a of total Cd^{2+} adsorption (cementation) (mM).

[c] Relative deviation (D) = $(N_{o,p} - N_{o,e})/N_{o,p}$ (%).

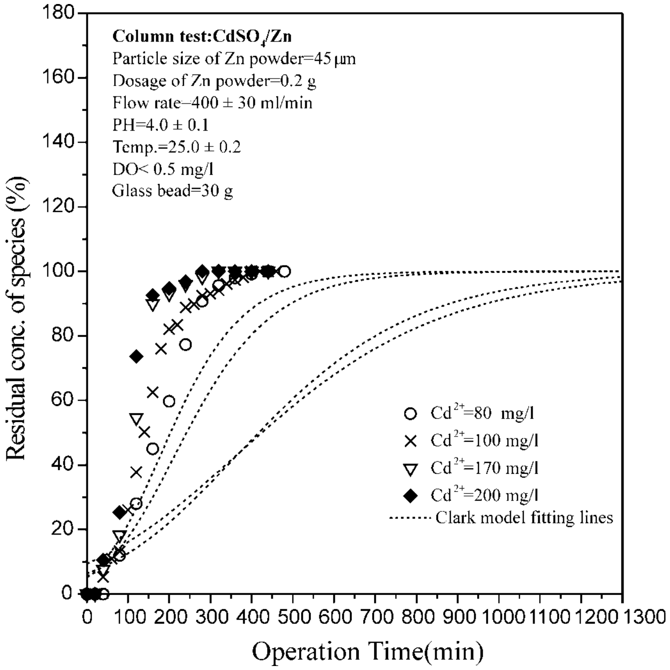

Figure 9. Experimental data and predicted simulations for the results of the effect of initial concentration of Cd^{2+} on the cementation rates of cadmium ions by the Clark model.

deviation (D) (60% ~ 85%) was observed among the three models and a very poor simulation outcome was obtained, as shown in Fig. 9, representing the three assumptions of this model could be doubtful. Comparing with the modeling results by the BDST model, it was revealed again that the cementation rate of cadmium ions in the zinc column is possibly determined by the surface reaction step rather than the outer mass-transfer step.

CONCLUSION

The experimental results showed that the cementation by using a zinc powder column is capable of efficiently recovering a medium level concentration of cadmium ions from aqueous solutions within a rather practical contact time. The efficiency of the utilization of a zinc powder bed improved with increasing empty bed contact time (EBCT), but the cementation capacity of zinc powder usually increased with decreasing EBCT value. The relationships between $t_{0.5}$ and zinc dosage, EBCT were correlated by the power law at the conditions in this work: $t_{0.5} = 2.626$ (zinc dosage)$^{0.706}$, and $t_{0.5} = 1.912$ (EBCT)$^{1.177}$. The breakthrough curve was found to extend and the effective cementation capacity of the zinc cementation column was raised by adding 10 ~ 20 μM SDS surfactant. The cementation behavior of cadmium ions in a zinc powder column can be well described by the BDST model rather than the Wolborska model and Clark model, indicating the cementation rate of Cd^{2+} by a cementation column test, which was mostly determined by the surface reaction step. The resulting effluent containing dissolved zinc can be recovered and should not be discarded without proper treatment to avoid further pollution problems.

NOMENCLATURE

A_c	cross area of column (m^2)
C_0	initial concentration of pollutants (mM)
C_A	effluent concentration of pollutants at t time (mM)
D	axial diffusivity coefficient of pollutants (cm^2/min)
G_s	flow rate per cross area (m^3/h)/m^2
H	distance from the column entrance (cm)
k_{ads}	second-order adsorption rate constant (L/min per mole)
k_m	outer mass-transfer coefficient of pollutants (min^{-1})
K_m	mass-transfer coefficient of pollutants (h^{-1})
K_e	equilibrium constants

M	dosage of absorbent (g)
N	equilibrium constants
N_o	total amount of adsorption capacity (mM)
q_o	adsorption capacity (mmole/g)
t	service time (min)
v	constant flow rate of the stream (mL/min)
v_m	velocity of stream (cm/min)

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REFERENCES

1. Gould, J.P.; Escover, I.B.; Khudenko, B.M. Examination of the zinc cementation of cadmium in aqueous solutions. Water Sci. Technol. **1987**, *19*, 333–335.
2. Agelidis, T.; Fytianos, K.; Vasikiotis, G.; Jannakoudakis, D. Lead recovery from aqueous solution and wastewater by cementation utilizing an iron rotating disk. Resour. Conserv. Recycl. **1989**, *2*, 131–137.
3. Anacleto, A.L.; Carvalho, J.R. Mercury cementation from chloride solution using iron, zinc, and aluminum. Miner. Eng. **1996**, *9* (4), 385–397.
4. Djokic, S.S. Cementation of copper by aluminum in alkaline solution. J. Electrochem. Soc. **1996**, *143* (4), 1300–1305.
5. Nosier, S.A.; Sallam, S.A. Removal of lead ions from wastewaters by cementation on a gas-sparged zinc cylinder. Sep. Purif. Technol. **2000**, *18*, 93–101.
6. Mahoud, A.Z. The effect of surface-active substance on the rate of production of copper powder from copper sulphate solution by cementation on zinc rods in gas sparged reactors. Hydrometallurgy **1996**, *41*, 231–242.
7. Owusu, G. Solvent Extraction of Copper from Zinc Sulphate Leach Solutions Using LIX 622 and the Effect of Organic Contamination on Zinc Electrowinning, EPD Congress TMS Annual Meeting, Minerals, Metals and Materials Society, 1998.

8. Karavasteva, M. The influence of copper on the effect of certain surfactants during the cementation of cadmium by suspended zinc particles. Hydrometallurgy **1998**, *48*, 361–366.
9. Karavasteva, M. The effect of certain surfactants on the cementation of nickel from zinc sulphate solutions by suspended zinc particles in the presence of copper. Can. Metallurgical Q. **1999**, *38* (3), 207–210.
10. Ku, Y.; Chen, C.H. Kinetic study of copper deposition on iron by cementation reaction. Sep. Sci. Technol. **1992**, *27* (10), 1259–1275.
11. Froment, G.F.; Bischoff, K.B. *Chemical Reactor Analysis and Design*; John Wiley and Sons: New York, NY, 1979.
12. Bohart, G.S.; Adams, E.Q. Some aspects of the behavior of charcoal with respect to chlorine. J. Am. Chem. Soc. **1920**, *42*, 523–544.
13. Hutchins, R.A. New method simplifies design of activated-carbon systems. Chem. Eng. **1973**, *80* (19), 133–138.
14. Wolborska, A. Cementation on activated carbon of p-nitrophenol from aqueous solution. Water Res. **1989**, *23* (1), 85–91.
15. Clark, R.M. Evaluation the cost and performance of field-scale granular activated carbon systems. Environ. Sci. Technol. **1987**, *21*, 573–580.
16. Ku, Y.; Wu, M.H.; Shen, Y.S. A study on the cadmium removal from aqueous solutions by zinc cementation. Sep. Sci. Technol. **2002**, *37* (3), 1–20.

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