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Cadmium and Copper Removal by a Granular Activated Carbon in Laboratory Column Systems

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ABSTRACT

Single and competitive removal of Cd and Cu from aqueous solutions by using Darco 12–20 mesh granular activated carbon in column systems has been investigated. Seven experiments modifying the initial pH and the flow rate were performed. Results showed the efficiency of activated carbon as a sorbent for both metals. pH is shown to be the decisive parameter on metal removal in the column; metal removal increases when the influent pH value is raised. The influence of the flow rate for the experimental conditions is negligible. Batch adsorption and column data are compared. Column modeling assuming local equilibrium and rate-controlled pore diffusion was performed.

Key Words. Activated carbon; Adsorption; Cadmium; Column; Copper

INTRODUCTION

Removal of heavy metals from aqueous wastes is a challenging task for the correct management of waste disposal. The effectiveness of adsorption onto activated carbon in removing heavy metals has been demonstrated (1–3). In order to evaluate adsorption process performance and to design new treatment

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units, predictions of the adsorbate partitioning between an aqueous solution and a solid surface are required. Such predictions can be achieved by an adequate modeling of the adsorption process. For this purpose, batch adsorption experiments are usually performed to obtain the distribution function of a solute between the solid and solution phases at equilibrium. Nevertheless, extrapolation of batch results to the prediction of removal capacities in column systems should be carefully evaluated, since differences in contact and flow conditions can result in discrepancies. Physical and chemical interactions during the adsorption process give rise to a release of different species from the solid phase. In batch systems the background composition of the liquid phase changes to a greater or lesser extent depending on both the solute and adsorbent concentrations. In column experiments which are performed at solid/solution ratios much higher than those used in batch systems, the released species are removed by the continuous flow of the mobile phase.

Solution pH has been identified as the main solution parameter controlling adsorption. pH affects not only the metal ion status (hydration, solubility, and solution speciation) but also the hydrolysis of surface-active groups. For most cationic heavy metals, the effect is an increase in metal removal with increasing pH. By increasing the solution pH, simultaneous precipitation can also contribute to heavy metal removal. Several authors (4, 5) have reported that surface/pore precipitation can occur in a adsorbent/solution system at pH values lower than those at which precipitation in a bulk solution occurs.

Cadmium and copper adsorption onto activated carbon Darco 12–20 mesh was studied in batch experiments in previous work (6). The influences of pH, cation concentration, and carbon concentration on metal removal were investigated. The experimental results were used for the calibration of parameters of the Freundlich adsorption isotherm, and a dependence on pH was obtained. Because of the influence of carbon concentration on heavy metal removal, column experiments were performed to check the possibility of prediction of adsorption equilibrium in continuous flow, high carbon/metal concentration systems.

Experimental and modeling results obtained in laboratory columns for cadmium and copper adsorption onto Darco 12–20 mesh granular activated carbon at different pHs and flow conditions are presented in this paper.

EXPERIMENTAL

Materials

The granular activated carbon used in this study was Darco 12–20 mesh supplied by Aldrich. Carbon was used without further washing, oven dried at 110°C for 24 hours, and then stored in a desiccator. The column experiments were performed on activated carbon sieved down to a fraction sized to less than 200 μm. Analytical grade reagents were used. Solutions of 1×10^{-4} M of the test metals were prepared by dilution of sulfate salts ($CuSO_4 \cdot 5H_2O$ and

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$CdSO_4 \cdot \frac{8}{3} H_2O$) with double distilled water. Solutions of 1×10^{-1} M NaOH and 1×10^{-1} M HCl were used for pH adjustment. A constant ionic strength of 1×10^{-2} M NaCl was used in all experiments as the background electrolyte as in batch experiments, and 1×10^{-2} M KCl was used as a conservative tracer for the calibration of the flow conditions.

Experimental Procedures

Two Pyrex glass columns of 22 cm length and 2.5 cm inner diameter were used in this study. End pieces were provided with 0.25 μm porous plaques. Columns were packed under water to avoid entrapping air by adding small quantities while gently tapping the sides of the column. The complete cycle of operation of each column experiment included three steps: pH precondition, tracer injection, and metal adsorption until column exhaustion occurred. Columns were operated in the up-flow mode. The feeding solution was pumped through the column by a Watson–Marlow model 101 U/R peristaltic pump with a variable flow rate in the 0.05–8.10 mL/min range. Two pH probes were inserted, one in the feeding tank and the other in a cell at the end of the column. pH was measured using a WTW combined electrode pHmeter model 3000 with ± 0.001 accuracy, equipped with a temperature probe and multiplex system 3000/pMX, connected to a PC for data accumulation. Effluent samples were collected by an automatic fraction collector, acidified with concentrated HNO_3, and stored for analysis. Metal concentration was measured using a Unicam model 939 Atomic Absorption Spectrophotometer. Experiments were carried out in a thermostatic room at 20.0 ± 0.5°C.

Three experiments were performed with freshly activated carbon for each metal. Two pH levels and two water flow velocities were investigated. An additional column run was conducted with a combined cadmium-copper feed. Table 1 summarizes the experimental conditions at each column run. To pre-

TABLE 1
Experimental Setup

Experiment	Cd^{+2} (M)	Cu^{+2} (M)	Influent pH	Flow rate (mL/min)	Carbon mass (g)	Bed porosity	Pore volume (mL)
1	1.07×10^{-4}		6.60	2.70	45.2	0.745	91.5
2	1.02×10^{-4}		6.40	5.54	44.7	0.728	86.0
3	9.78×10^{-5}		4.70	2.98	40.0	0.757	88.9
4		7.99×10^{-5}	6.50	2.72	43.4	0.754	88.9
5		9.65×10^{-5}	4.80	5.53	40.7	0.689	81.6
6		9.23×10^{-5}	4.70	2.57	30.8	0.795	63.7
7	9.32×10^{-5}	9.76×10^{-5}	4.70	2.67	31.9	0.791	64.7

condition the column, a distilled water feed containing the background electrolyte (0.01 M NaCl) adjusted to the appropriate pH was pumped through at the experimental flow rate. Effluent pH was measured and the column was considered pretreated when pH differences between influent and effluent were smaller than 0.05 pH units. The precondition step was a slow process collecting 1000 to 2000 pore volume of effluent. Tracer solution containing 0.01 M KCl with the pH adjusted to the pH of the pretreated column was fed to the column until breakthrough occurred. At that moment the feed used in the pre-

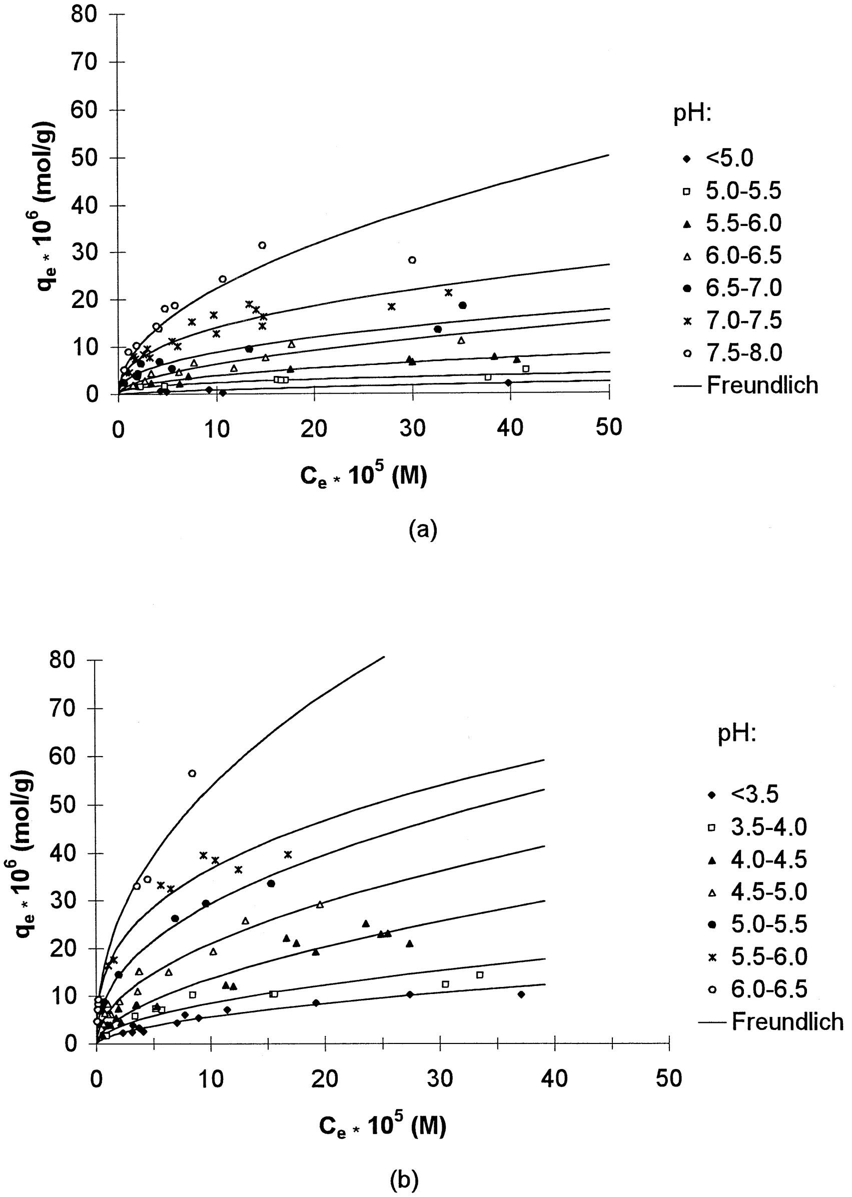

FIG. 1 Experimental batch adsorption data onto activated carbon Darco 12–20 mesh and Freundlich isotherms for (a) Cd and (b) Cu (6).

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condition step was introduced to the column until complete elution of KCl was achieved. To start the adsorption experiment, 10^{-4} M metal solution with 0.01 M NaCl was pumped into the column. The pH of the influent was adjusted to the pH of the pretreated step, monitored, and controlled with an error of ±0.05 pH units. Effluent aliquots of approximately 10 mL were collected every 60 minutes and measured for metal content. The column was run until the effluent pH was stabilized at its initial value, at which point it was assumed that complete breakthrough had been obtained. The volumetric water content of the packed columns was determined from the water volume collected by the inversion of flow at the end of the experiment plus the difference in weight of drained and oven-dry columns at 105°C. The bed porosities obtained for each column run are presented in Table 1, along with the pore volumes.

RESULTS AND DISCUSSION

Batch Experiments

Batch adsorption experiments were performed in a wide variety of conditions including different pHs, in ranges of 4.0–8.0 for cadmium and 3.0–6.5 for copper, various metal concentrations (4×10^{-5} to 2×10^{-3} M), and carbon concentrations in the 5–20 g/L range. Experimental and modeling procedures were presented in previous work (6). Our experimental results along with predictions with the adsorption isotherm are presented in Fig. 1. The results show typical cation adsorption behavior, with higher adsorption for increasing pH. The isotherms are nonlinear, and each can be described by a Freundlich isotherm, $q_e = K_F c^{1/n}$. The determination of the parameters of the Freundlich adsorption isotherm resulted in a pH dependence and are summarized in Table 2.

TABLE 2
Freundlich Adsorption Isotherm for Cadmium and Copper onto Activated Carbon Darco 12–20 Mesh from Batch Adsorption Data (6)

Cadmium				Copper			
pH	K_F [(mol/g)(mol/L)^n]	n	r^2	pH	K_F [(mol/g)(mol/L)^n]	n	r^2
<5.0	2.66×10^{-4}	1.630	0.942	<3.5	1.08×10^{-3}	1.758	0.910
5.0–5.5	5.94×10^{-5}	2.893	0.893	3.5–4.0	1.13×10^{-3}	1.888	0.934
5.5–6.0	3.13×10^{-4}	2.108	0.943	4.0–4.5	2.60×10^{-3}	1.756	0.966
6.0–6.5	9.10×10^{-4}	1.858	0.915	4.5–5.0	2.02×10^{-3}	2.018	0.956
6.5–7.0	4.52×10^{-4}	2.346	0.938	5.0–5.5	1.61×10^{-3}	2.298	0.998
7.0–7.5	5.73×10^{-4}	2.487	0.912	5.5–6.0	9.37×10^{-4}	2.842	0.952
7.5–8.0	2.25×10^{-3}	1.998	0.936	6.0–6.5	3.18×10^{-3}	2.257	0.988

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Column Experiments

Influence of pH and Flow Rate on Metal Breakthrough

The normalized effluent metal concentration, C/C_0, versus the number of pore volumes treated (breakthrough curves) are presented in Fig. 2 for Cd and Fig. 3 for Cu transport experiments. The effects of pH and water flow rate are shown. The breakthrough curves present a similar shape in all cases: an initial rapid increase in the normalized concentration followed by an abrupt change in the shape before slowly reaching column exhaustion ($C/C_0 = 1$). The asym-

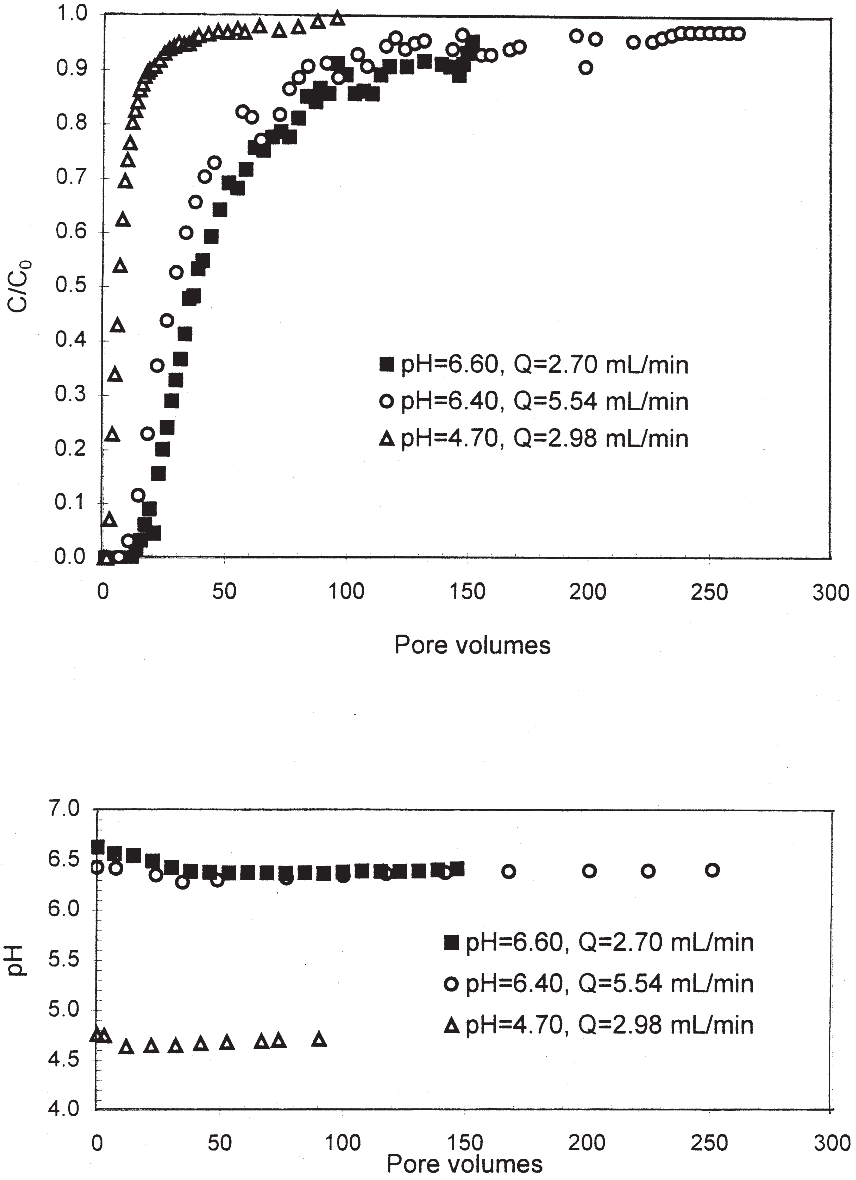
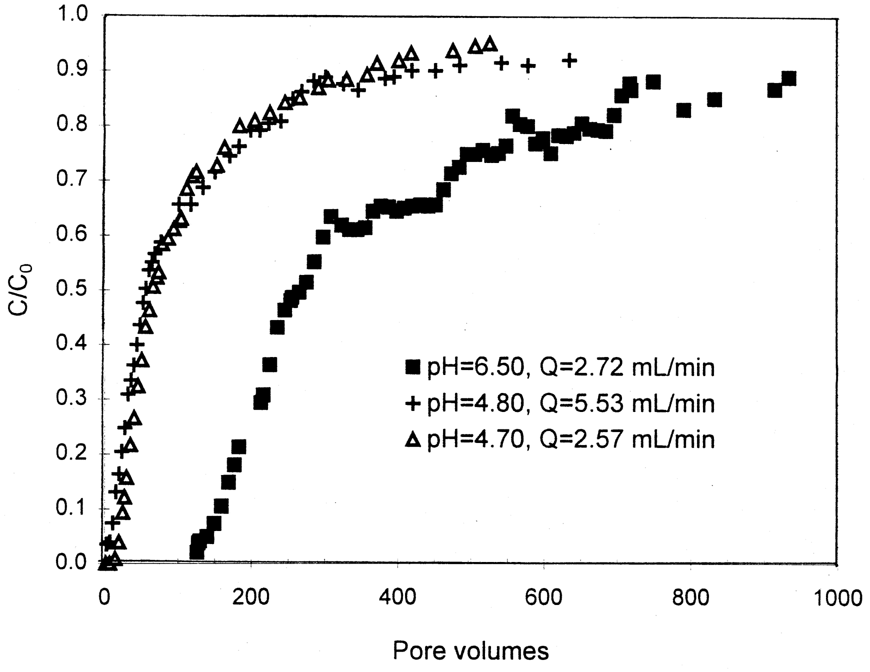


FIG. 2 Experimental Cd breakthrough and effluent pH curves (Experiments 1, 2, and 3).



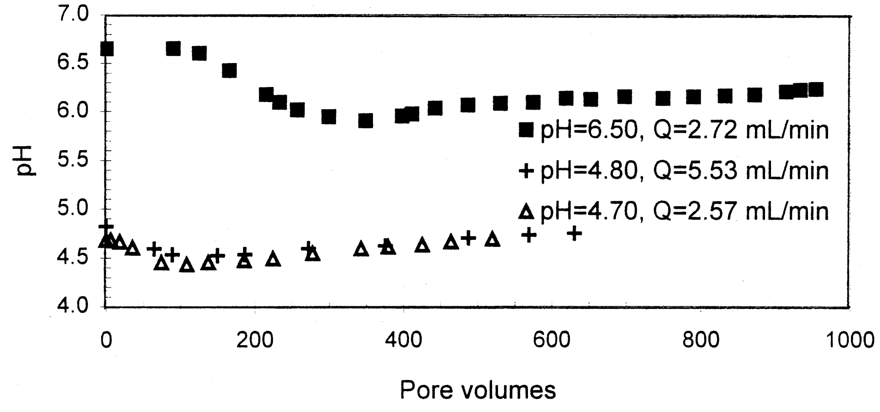


FIG. 3 Experimental Cu breakthrough and effluent pH curves (Experiments 4, 5, and 6).

metry of the curves, with early breakthrough and tailing, reveals nonideal transport (7).

The effluent pH versus the number of pore volumes has been also plotted. As can be observed, the effluent pH remains at approximately a constant value within 0.2 pH units for Cd column runs and 0.5 pH units for Cu experiments.

To observe the metal breakthrough curve, it was necessary to leach the column with a large number of pore volumes of the feeding solution, indicating strong retention of the tested heavy metals onto Darco 12–20 mesh activated carbon. The number of pore volumes needed to reach 90% of column exhaustion varied from 20 at influent pH 4.70 to 120 at influent pH 6.60 in the case of Cd and from 300 at influent pH 4.70 to 700 at influent pH 6.50 in the case of Cu. As could be expected from the batch adsorption data (Fig. 1), Cu retention is higher than Cd retention at the same pH, indicating a greater affinity of the activated carbon Darco 12–20 mesh for Cu than for Cd. The pH is the decisive factor for metal removal. An increase in retardation at higher pH was observed due to the dependence of metal adsorption on pH.

For the two flow rates used, 2.6–3.0 and 5.5 mL/min, the breakthrough curves obtained for similar influent pH conditions are nearly superposed for Cu. In the case of Cd, the discrepancies observed can be related more to the difference in 0.2 units in the influent pH than to the flow rate. The absence of a significant influence of flow rate on the breakthrough curve indicates that retardation effects associated with dispersive transport and possible adsorption rate-limited processes are of the same order on the time scale of the column experiments for the flow rate range used.

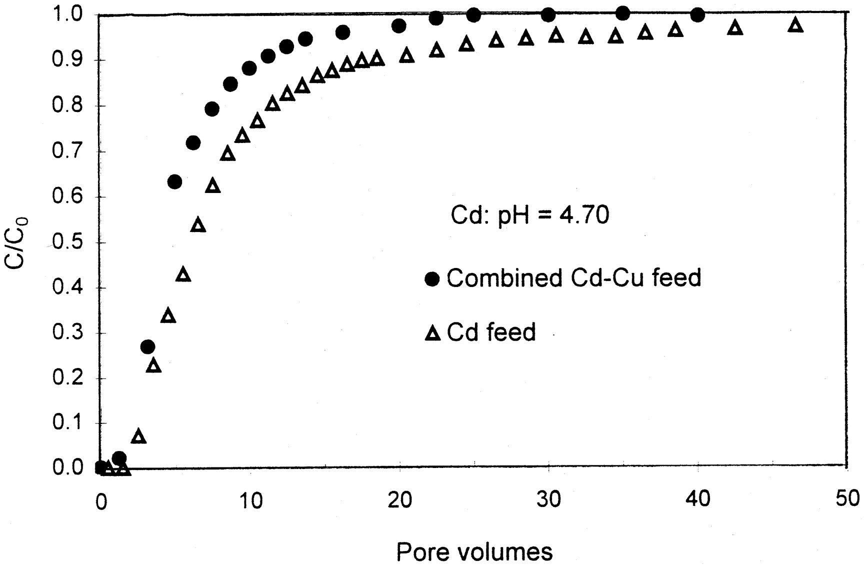
Similar effluent pH curves have been obtained for all experiments, with a decrease in pH followed by a slow stabilization to the influent pH boundary condition. pH decreases because H^+ is released as the metal adsorbs, as was previously reported for the adsorption of heavy metals onto hydrous solids (5). As adsorption proceeds to column exhaustion, H^+ release diminishes, creating a pH profile heading to ward the influent pH. The minimum pH value corresponds in all cases to a breakthrough C/C_0 value of approximately 0.7.

Effect of Competitive Adsorption

A column experiment with a combined Cd-Cu feed at pH 4.70 was performed to evaluate the influence of multicomponent adsorption on metal removal efficiency. The results are shown in Fig. 4 along with the metal breakthrough curves obtained for individual column runs. As can be observed, the Cu breakthrough curve is essentially unaffected by the presence of Cd. Figure 4 also illustrates that the presence of Cu decreases the amount of adsorbed Cd. Cd retention in this experiment has been evaluated in 64% less than in the individual Cd transport experiment. Thus, the binary system shows competition for the available adsorption surface sites. Cu, which is more strongly attracted to activated carbon, decreases Cd retention.

Comparison of Adsorption in Column and Batch Experiments

The extent of adsorption in column and batch experiments can be compared from the adsorption isotherm applied to the column exhaustion point. The metal retained in the column has been calculated from the area above the breakthrough curve up to the experimental column end point. The results are



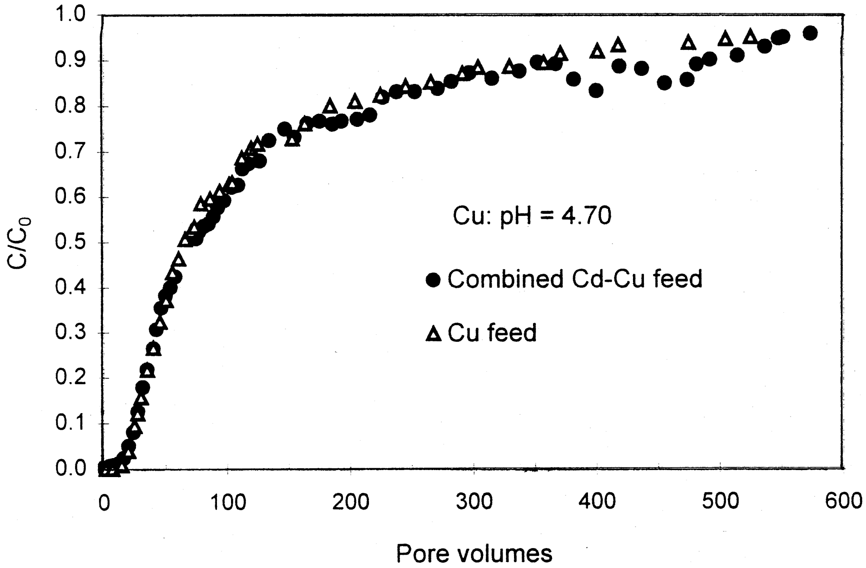


FIG. 4 Experimental breakthrough curves for individual and competitive adsorption. Top: Cd (Experiments 3 and 7). Bottom: Cu (Experiments 6 and 7).

summarized in Table 3 along with the predicted metal adsorption capacity from batch isotherms. In the case of Experiment 3, adsorption isotherm parameters have been recalculated in the 4.5–5.0 pH range, instead of the previously reported isotherm for pH $<$ 5 which included data up to pH 4. In all cases the batch adsorption isotherms underestimate the metal retention ob-

TABLE 3
Comparison of Metal Retention in Column and Predicted Batch Adsorption Removal

		Prediction from batch adsorption data at $C/C_0 = 1$			
		Freundlich adsorption isotherm			
Experiment	Column end point, metal removal (mg)	pH range	K_F [(mol/g) (mol/L)^n]	n	Metal removal (mg)
1-Cd	58.04	6.5–7.0	4.52×10^{-4}	2.346	46.62
2-Cd	46.07	6.0–6.5	9.10×10^{-4}	1.858	32.50
3-Cd	10.72	4.5–5.0	1.80×10^{-4}	1.904	6.34
4-Cu	173.85	6.0–6.5	3.18×10^{-3}	2.257	134.14
5-Cu	68.50	4.5–5.0	2.02×10^{-3}	2.018	53.48
6-Cu	46.68	4.5–5.0	2.02×10^{-3}	2.018	39.59

served in column experiments. Relative deviations range from 20 to 40% for Cd and from 15 to 22% for Cu, the higher values corresponding to the lowest pH.

Such discrepancies may be explained on the basis of a combined removal mechanism including adsorption and perhaps surface precipitation processes. Surface precipitation in metal-activated carbon systems has been previously reported (5). According to Reed et al., possible reasons for surface precipitation may be: the surface pH is higher than the solution pH; the surface acts as a nucleus for metal hydroxide precipitation; OH^- accumulates in the carbon pores. These effects may become higher as the adsorbate concentration approaches to the saturation concentration. In any case, surface precipitation was not observed in batch adsorption experiments.

Clancy and Jennings (8) reported similar deviations between batch and column data for the single and multicomponent transport of Cd and Zn onto Sassafras soils: “sorption parameters measured under static conditions underestimated the attenuation capacities observed during dynamic transport.” These authors concluded that particular environmental conditions on column studies produced specific interactions between solutes and soil at high soil/solution ratios.

Column Modeling

Solute transport simulation assuming local equilibrium was performed in the first stage. For one-dimensional transport in the positive z direction with steady-state flow, the convection-dispersion equation is

$$\theta \frac{\partial c}{\partial t} + \rho \frac{\partial q}{\partial t} = \theta D \frac{\partial^2 c}{\partial z^2} - \theta v \frac{\partial c}{\partial z} \tag{1}$$

where θ is the bed porosity, c is the solute concentration ($M\cdot L^{-3}$), ρ is the bulk density of the porous media in the column ($M\cdot L^{-3}$), q represents the adsorbed amount ($M\cdot M^{-1}$), D is the hydrodynamic dispersion coefficient ($L^2\cdot T^{-1}$), and v is the average pore water velocity ($L\cdot T^{-1}$). For the local equilibrium assumption, q is evaluated from the Freundlich isotherm at the corresponding column pH range, as shown in Table 3. The hydrodynamic dispersion coefficient was estimated from tracer experiments, resulting in 2×10^{-6} and 5×10^{-6} m^2/s for water flow rates of 2.6–3.0 and 5.5 mL/min, respectively. Nonideal conservative solute transport was observed, indicating that solute access to portions of the porous medium can be constrained by diffusive mass transfer.

Results of Cd and Cu local equilibrium transport simulation are shown in Figs. 5 and 6, respectively. In all cases the simulated breakthrough curves do not represent the early breakthrough and tailing of the experimental data due to overprediction of the initial metal retardation. Such a discrepancy reveals that mass transfer limitations superposed to advective-dispersive transport cause the nonideality of experimental transport.

Rate-controlled simulations assuming pore diffusion limitation where performed. Pore diffusion was modeled by first-order kinetics with a linear driving force. Thus, system equations for solute transport assuming pore diffusion mass transfer rate control are Eq. (1) plus

$$\partial q/\partial t = K_p(q_e^* - q) \qquad (2)$$

where K_p is the first-order mass transfer coefficient (T^{-1}). In this case, q_e^* represents the adsorbed concentration at the external surface of the adsorbent, in equilibrium with the adsorbate solution concentration, and q represents the average adsorbed concentration. Transport simulations were performed to estimate the mass transfer coefficient directly from transport data. Results are shown in Figs. 5 and 6 for both metals. The mass transfer coefficients range from 6×10^{-5} to 4×10^{-4} s^{-1} for Cd and 2×10^{-5} to 5×10^{-5} s^{-1} for Cu. The mass transfer coefficients of Experiments 5 and 6 shown a nondependence on flow rate. From the mass transfer coefficients of Experiments 1 and 3, or 4 and 6, a dependence of K_p on pH is observed. Diffusion is slower as pH increases, indicating an increase in the molecular size of the metal hydroxylated-complexes to be adsorbed. The smaller values of K_p obtained for Cu seem to indicate that kinetic effects are more important for the most retained species.

The predicted simulations matched the experimental data quite well up to the tailing of the breakthrough curves, but it is not possible to simulate the final zone of the breakthrough curve due to the increase in metal removal from batch data. The results seem to indicate that an additional removal mechanism not explained by the adsorption isotherm, but probably negligible at a low ad-

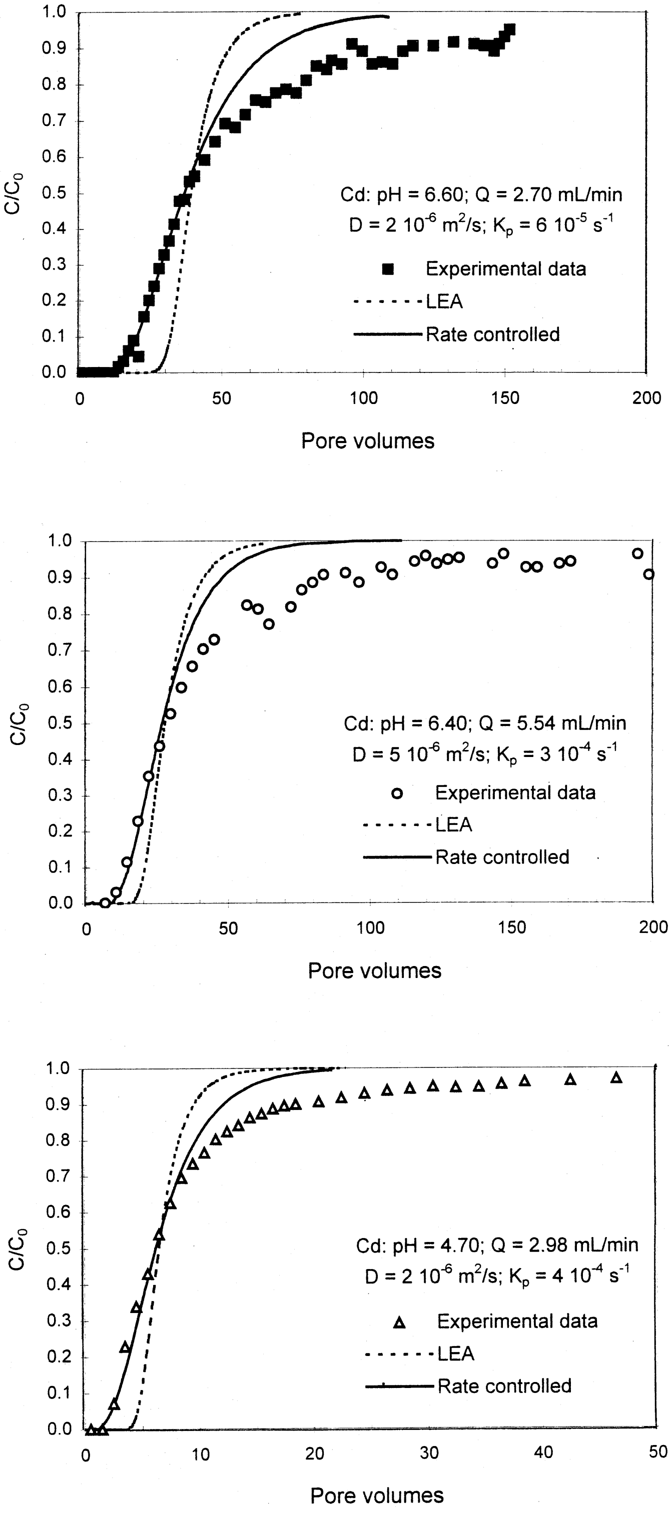


FIG. 5 Experimental data and predicted simulations for local equilibrium adsorption model and first-order pore diffusion rate-control model for Cd transport (Experiments 1, 2, and 3).

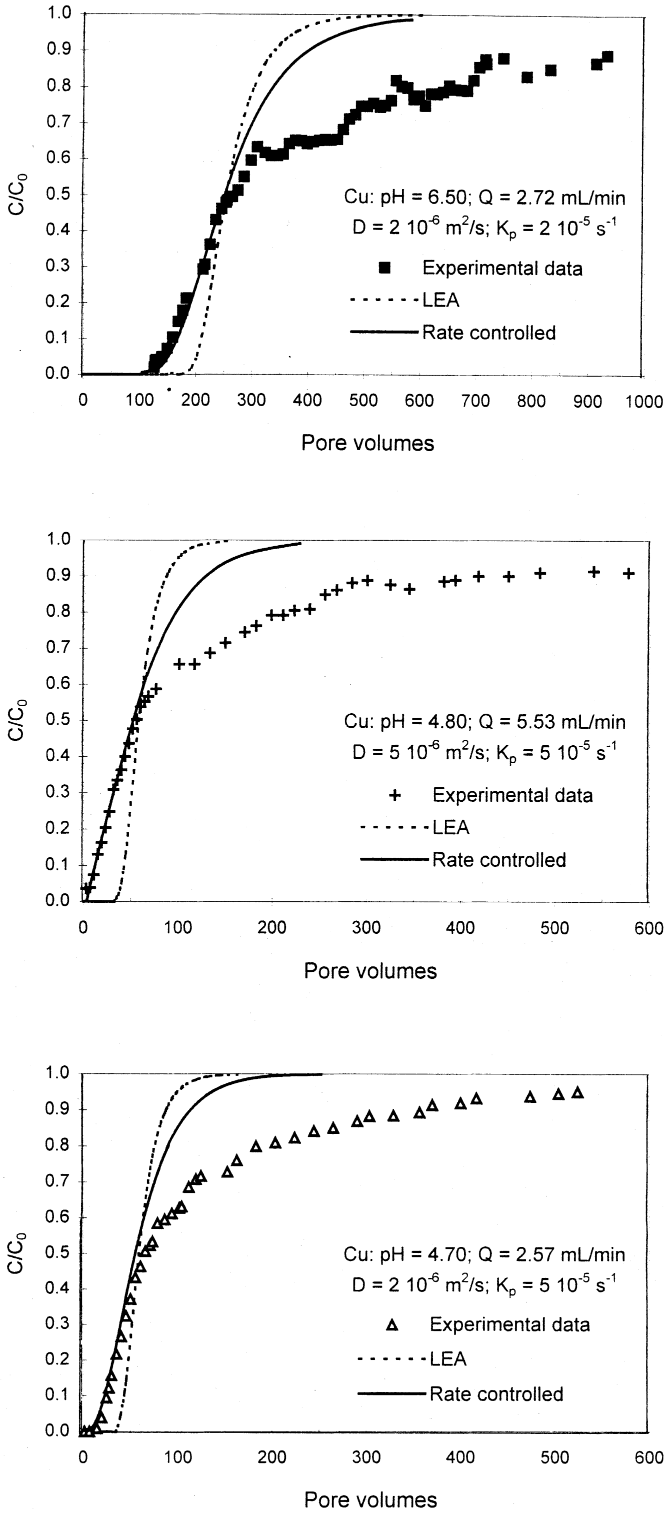


FIG. 6 Experimental data and predicted simulations for local equilibrium adsorption model and first-order pore diffusion rate-control model for Cu transport (Experiments 4, 5, and 6).

sorbed metal concentration, becomes a decisive retention factor as the column tends to saturation.

CONCLUSIONS

Cadmium and copper removal onto Darco 12–20 mesh granular activated carbon in continuous flow systems has been investigated. Metal removal showed a decisive dependence on influent solution pH, and a nondependence on water flow rate for our experimental conditions. Cu is more strongly retained than Cd at the same pH, as could be expected from previous batch adsorption data. In binary transport the presence of Cu decreases the capacity of the activated carbon to retain Cd. Otherwise, Cd has no effect on the removal of Cu.

Metal retentions in column in all cases were much higher than the removal expected based on batch adsorption isotherms. These results indicate that the same removal mechanisms do not occur in batch and transport experiments. For the systems studied, which are characterized by a strong adsorption capacity with high metal concentrations, using batch extrapolation results for the prediction of removal capacities in column systems is not possible. Predicted simulations based on the assumption of pore diffusion rate-control conditions matched the experimental data in the initial zone of the breakthrough curves, but not in the final tailing zone. This indicates that specific interactions between solutes and carbon which increase metal removal from adsorption equilibrium seem to become decisive retention factors as the column tends to saturation.

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