Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Seco, Aurora , Marzal, Paula , Gabaldón, Carmen and Ferrer, José(1999) 'Study of the Adsorption of Cd and Zn onto an Activated Carbon: Influence of pH, Cation Concentration, and Adsorbent Concentration', Separation Science and Technology, 34: 8, 1577 — 1593

To link to this Article: DOI: 10.1080/01496399909353758

URL: http://dx.doi.org/10.1080/01496399909353758

SEPARATION SCIENCE AND TECHNOLOGY, **34**(8), pp. 1577–1593, 1999

Study of the Adsorption of Cd and Zn onto an Activated Carbon: Influence of pH, Cation Concentration, and Adsorbent Concentration

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ABSTRACT

The single adsorption of Cd and Zn from aqueous solutions has been investigated on Scharlau Ca 346 granular activated carbon in a wide range of experimental conditions: pH, metal concentration, and carbon concentration. The results showed the efficiency of the activated carbon as sorbent for both metals. Metal removals increase on raising the pH and carbon concentration, and decrease on raising the initial metal concentration. The adsorption processes have been modeled using the surface complex formation (SCF) Triple Layer Model (TLM). The adsorbent TLM parameters were determined. Modeling has been performed assuming a single surface bidentate species or an overall surface species with fractional stoichiometry. The bidentate stoichiometry successfully predicted cadmium and zinc removals in all the experimental conditions. The Freundlich isotherm has been also checked.

Key Words. Activated carbon; Adsorption; Cadmium; Zinc; Triple layer model

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INTRODUCTION

The toxicity of heavy metals released into the environment has increased the number of studies concerning heavy metals removal from aqueous solutions over recent years. Adsorption onto different carbonaceous materials (activated carbon, peat, lignite) has become an accepted method for heavy metals removal (1–3). Both to evaluate the process performance and to design new treatment units, predictions of the metal partitioning between the aqueous solution and the solid surface are required. Such predictions can be achieved by an adequate modeling of the adsorption process. Heavy metal adsorption equilibrium has been modeled by using the classical empirical adsorption isotherms (Linear, Langmuir, Freundlich) or by applying mechanistic models such as surface complex formation (SCF) models (4). The adsorption equilibrium studies have consistently revealed that pH is the dominant solution parameter controlling adsorption, which limits the applicability of the isotherms since adsorption parameters must be determined at constant pH. On the other hand, the more general SCF models incorporate the complexity of the aqueous chemistry and the specific interactions between the surface of the solid and the metal ion by taking into account the effects of pH, solution composition, and other factors. However, the application of SCF models to activated carbon systems is still limited due mainly to the scarcity of information related to the model definition and calibration. Since the predicted responses can be highly dependent on the model formulation, model calibration involves the selection of a set of possible surface species, not always previously identified. Therefore, experimental data obtained in a wide range of solid-solution conditions, including different pHs and adsorbent and adsorbate concentrations, should be required for the model fit, and modeling efforts involving a complete set of experimental data are still scarce.

The objective of this study was to investigate the adsorption characteristics of two heavy metals, cadmium and zinc, onto a commercial granular activated carbon (Scharlau Ca 346). The activated carbon used is an L-type carbon adequate for cation adsorption. The experiments have been performed to study the effects of such important factors as pH, metal concentration, and carbon concentration on heavy metals removal in a wide range of experimental conditions. The SCF Triple Layer Model (TLM) (5) has been used to predict heavy metal adsorption onto activated carbon. For this purpose, a preliminary characterization of the adsorbent was required. Hence, the specific surface area of the adsorbent and its acid–base behavior were also determined. Modeling procedures presented in this work are an additional contribution in a research project studying the adsorption processes of different heavy metals onto several granular activated carbons in both batch and column systems (6–9).

EXPERIMENTAL

The granular activated carbon used in this study was Ca 346 supplied by Scharlau (La Jota, 86-08016 Barcelona, Spain). The activated carbon was used without further washing, oven dried at 110°C for 24 hours, and then stored in a desiccator. Analytical grade reagents were used. Stock solutions of 1×10^{-2} M of the test metals were prepared by dilution of sulfate salts ($ZnSO_4 \cdot 7H_2$) and $CdSO_4 \cdot {}^8/_3H_2O$) with double distilled water. Solutions of 1×10^{-1} M NaOH and 1×10^{-1} M HCl were used for pH adjustment in both batch and titration experiments. The ionic strengths of the solutions were adjusted in all experiments, using NaCl as the background electrolyte.

Characterization of the Activated Carbon

The surface area was determined by the nitrogen BET method (10). The pore site distribution was determined by the BJH method (11). Acidimetric-alkalimetric titrations were performed using a microburet. pH measurements were monitored with a WTW combined electrode pHmeter model 3000 with ±0.003 accuracy, equipped with a temperature probe. Samples of a 100 g/L suspension of activated carbon were closed to the atmosphere, and a period of 24 hours was used to equilibrate the suspension pH prior to titration. The titrations were performed at four ionic strengths: 0.001, 0.01, 0.05, and 0.2 M NaCl, and at room temperature (20–22°C). A 5-minute period between each titration addition was used. Blank samples containing only NaCl were also titrated.

Batch Adsorption Experiments

All experiments were carried out at constant 0.01 M NaCl ionic strength and at 20°C. For each metal the experiments were designed to study the influence of pH, metal concentration, and carbon concentration on the adsorption process. For this purpose the adsorption of cadmium and zinc under several metal concentrations for a constant carbon dose was studied in the 4–8 equilibrium pH range. Three carbon doses in the 5–20 g/L range were employed. Additional experiments with carbon concentrations of 40 and 100 g/L were also performed for the Ca 346–Zn system. For this granular activated carbon, 100 g/L is the maximum concentration that can be handled in batch experiments.

Batch adsorption experiments were conducted by mixing 50-mL solutions, containing one metal, with a constant dose of activated carbon (0.25, 0.5, 1, 2, or 5 g) in 100-mL Pyrex Erlenmeyer flasks with cap. Flasks were shaken (180 rpm) at constant temperature using a New Brunswick Scientific G25KC model incubator orbital shaker with temperature control in the 4 to 60°C range.

The adsorption of Cd or Zn from solutions with heavy metal concentrations from approximately 2 × 10^{-5} M to 2 × 10^{-3} M was performed. For each metal concentration, one sample was reserved for analysis to determine the initial metal concentration in the flasks, and 6–8 samples were prepared with different initial pH values by the addition to each flask of predetermined amounts of 1 × 10^{-1} M HCl or 1 × 10^{-1} M NaOH. The reaction period lasted 72 hours, which was previously verified as being time enough to ensure that equilibrium conditions were reached. At the end of the reaction period, pH was measured using the WTW combined electrode pHmeter model 3000. Samples were filtered with a Millipore filter and filter holders (25 mm diameter, 1.2 mm pore size). Filtrates were collected in bottles and acidified with concentrated HNO_3. The residual metal concentration in the supernatant was measured using a Unicam model 939 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Characterization of the Activated Carbon

The specific surface area of the activated carbon Scharlau Ca 346 mesh obtained from two replicates was 838 m^2/g. Total pore volume was 0.58 cm^3/g and BJH pore volume of pores between 17.0 and 300.0 Å was 0.23 cm^3/g.

The experimental titration curves of the adsorbent are shown in Fig. 1. An estimation of the surface site density of the adsorbent can be obtained from the maximum proton uptake or release by the adsorbent at extreme pH values since it represents the concentration of ionizable hydroxyl groups (4). Hence, both sample and blank titrations were carried out up to extreme pH values (1 to 13), with the surface site density being evaluated from the titrant consumption at the intercept point between sample and blank curves. At this point it was assumed that all the ionizable hydroxyl groups of the sample have been titrated. From the four titrations performed, both in acidic and basic zones, an average surface site density of 3.80 × 10^{-6} mol/m^2 was estimated.

The single-diprotic-weak acid model was adopted to represent the acid–base behavior of the carbon surface (6, 12–14). According to TLM, two surface acidity constants are defined by mass action laws, including an electrostatic correction term:

$$K_{1a} = \frac{[\underline{C}OH][H^+]}{[\underline{C}OH_2^+]} \exp(-F\Psi_o/RT) \qquad (1)$$

$$K_{2a} = \frac{[\underline{C}O^-][H^+]}{[\underline{C}OH]} \exp(-F\Psi_o/RT) \qquad (2)$$

where K_{1a} and K_{2a} are the surface acidity constants; $[\underline{C}OH_2^+]$, $[\underline{C}O]$, and $[\underline{C}OH]$ are the concentrations of positively charged, negatively charged, and

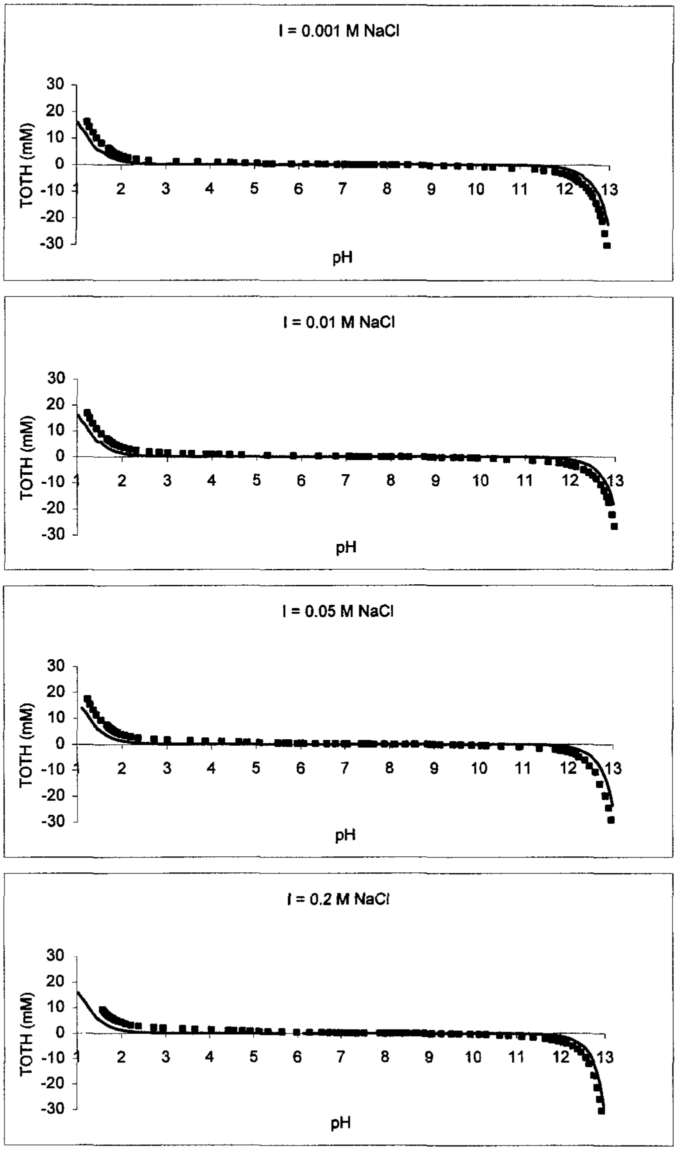


FIG. 1 Titration curves of 100 g/L suspension of activated carbon Scharlau Ca 346 at 0.001, 0.01, 0.05, and 0.2 M NaCl ionic strengths. TOTH indicates added titrant concentration (mM). (■) Adsorbent titration, (——) blank.

neutral surface sites; $[H^+]$ is the proton concentration in the bulk solution; R, F, and T are the gas constant, Faraday constant and absolute temperature, respectively; and ψ_o is the electrostatic potential at the o-plane. K_{1a} and K_{2a} were calculated by applying the double extrapolation method as described by Kent et al. (15). This method requires calculation of the following quantities:

$$pQ_+ = pH + \log\frac{a_+}{1-a_+}; \qquad pQ_- = pH - \log\frac{a_-}{1-a_-} \tag{3}$$

where a_+ and a_- are the fraction of the positively and negatively charged sites, respectively. These fractions were obtained from the net surface charges, $+\sigma_0$ for pH values lower than zpc (zero point of charge) and $-\sigma_0$ for the higher than zpc ones, as:

$$a_+ = \frac{+\sigma_0}{N_s b}; \qquad a_- = \frac{-\sigma_0}{N_s b} \tag{4}$$

where N_s represents the surface site density (mol/m^2) and b is the conversion factor from molar to electrostatic units. The net surface charge, σ_0, is here defined as

$$\sigma_0 = (F/AS)\,(C_a - C_b - [H^+] + [OH^-]) \tag{5}$$

in which A is the specific surface area, S is the solid concentration, and C_a and C_b are the molar concentrations of the acid and base added. $[H^+]$ and $[OH^-]$ are calculated from the titration pH measurements.

The intercept of the extrapolated curves pQ_+ vs $a_+ + 0.05(I)^{0.5}$ and pQ_- vs $a_- + (I)^{0.5}$ (Fig. 2) at $a_+ \rightarrow 0$ and at ionic strength $(I) \rightarrow 0$, and at $a_- \rightarrow 0$ and at $I \rightarrow 0$ becomes equal to pK_{1a} and pK_{2a}, respectively. The experimental values obtained obtained were 3.48 for pK_{1a} and 11.54 for pK_{2a}, resulting in a pH_{zpc} of 7.51.

The adsorbent characteristics determined in this section, specific surface area, surface site density, and acid–base constants, have been used in the application of TLM to modeling of the metal adsorption experiments.

Batch Adsorption Experiments

pH–metal removal curves at carbon doses of 5, 10, and 20 g/L are presented in Figs. 3 and 4 for Cd and Zn, respectively. Zn pH-removal curves at carbon doses of 40 and 100 g/L are presented in Fig. 5. The experiments were carried out for pH values below the pH where chemical precipitation of the metal hydroxides occurs. In these conditions, metal removal can be related only to the adsorption process.

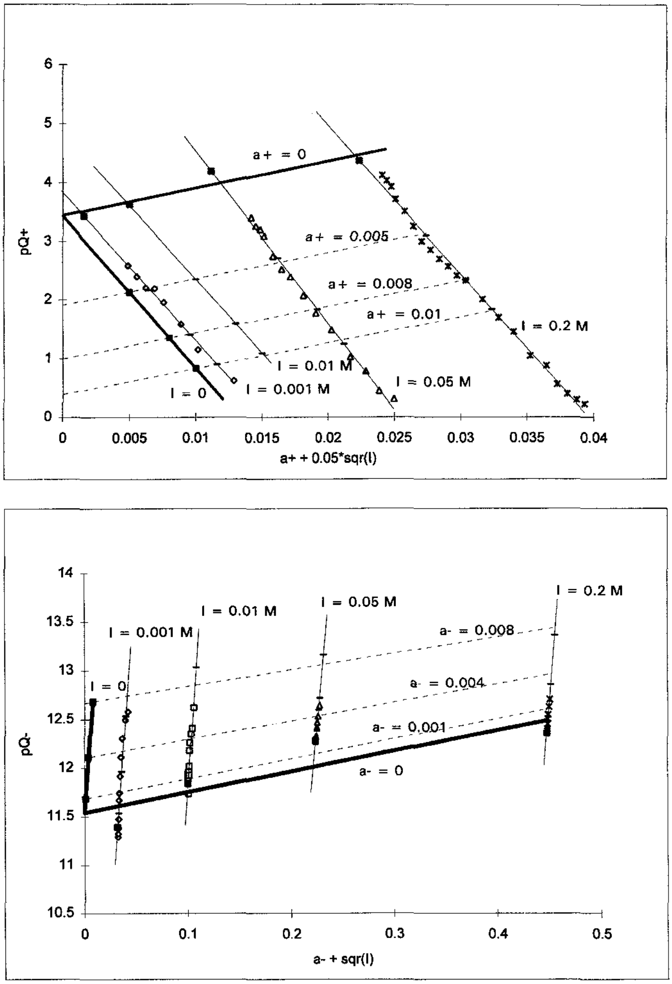
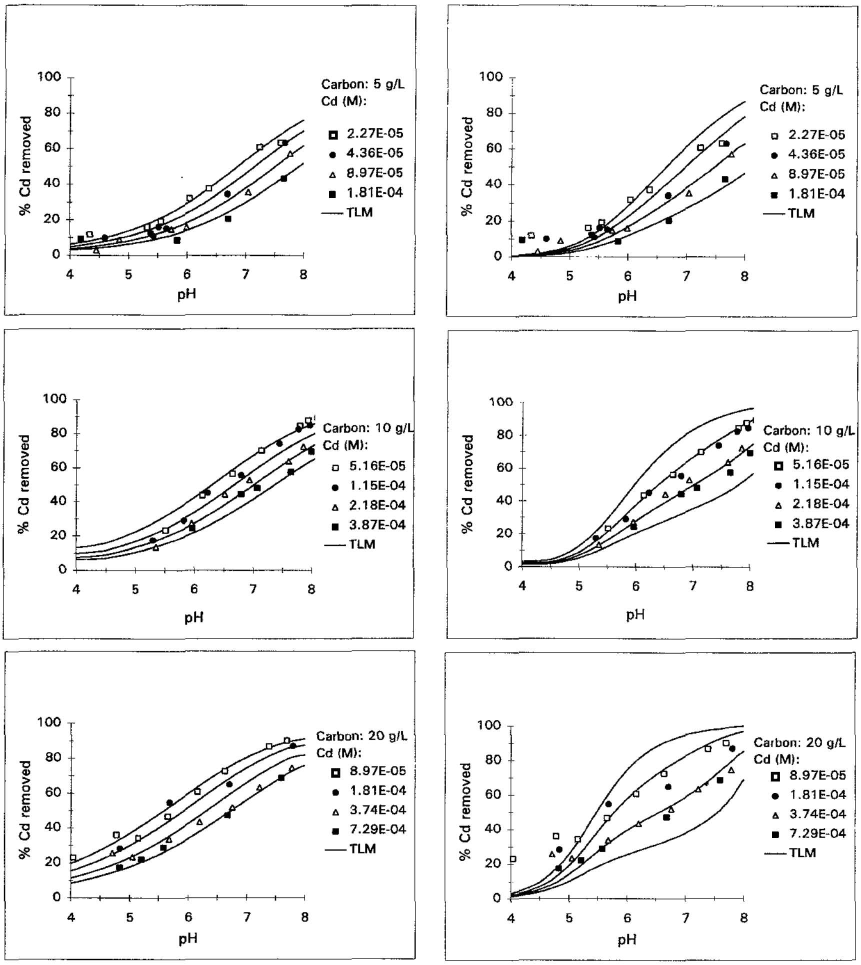


FIG. 2 Double extrapolation method used for the estimation of pK_{1a} and pK_{2a} from titration data.

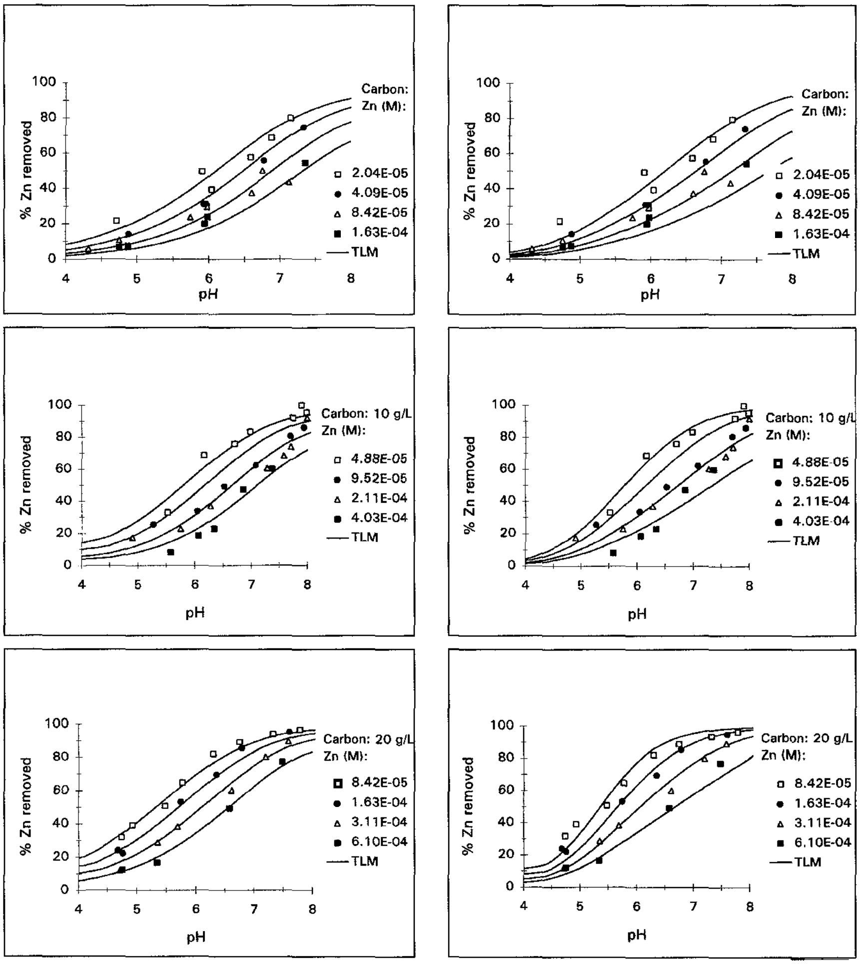
Metal removal is strongly dependent on pH. Cd and Zn removals increased from zero to 100% in a narrow pH range (3–4 pH units), with the greatest adsorption occurring at the highest pH values. According to SCF theory, the increase in metal removal as pH increases can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower coulombic



(a) (b)

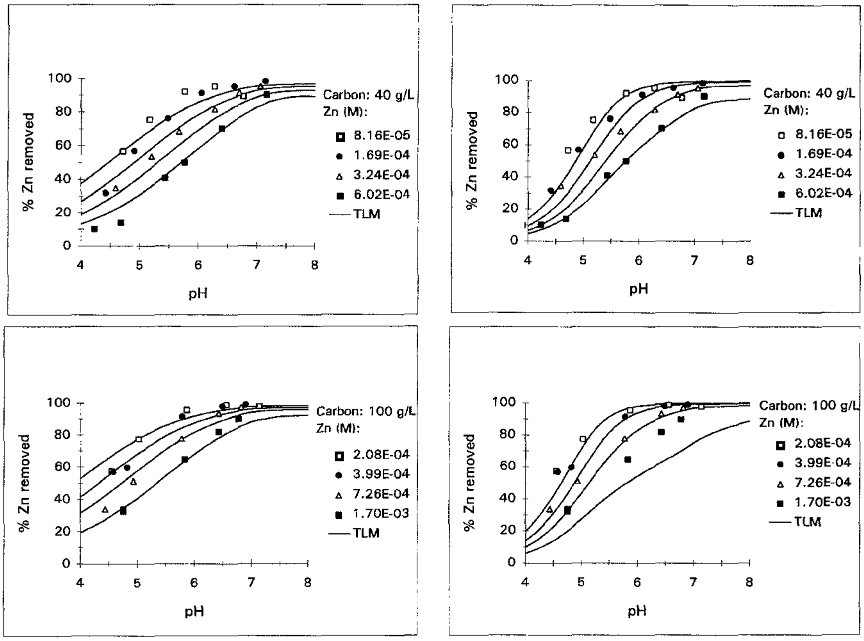
FIG. 3 Experimental cadmium pH adsorption edges at various cadmium and carbon concentrations. (a) TLM calibration results for bidentate stoichiometry. (b) TLM calibration results for fractional stoichiometry.

repulsion of the sorbing metal. As can be observed by comparison of the experimental data plotted in Figs. 3 and 4, Zn presents a greater removal percentage than Cd at the same pH, metal, and carbon concentrations. The preference of several hydrous solids for metals has been related to the equilibrium constant of the first metal hydrolysis reaction (4, 14). The reported effect is a stronger attraction for the metal showing a higher first hydrolysis equilibrium constant. The hydrolysis equilibrium p*K* values are 8.96 for $ZnOH^+$ and 10.08 for $CdOH^+$ (16). Therefore, the tendency observed for activated carbon Scharlau Ca 346 is in agreement with those previously reported for other hydrous solids.



(a) (b)

FIG. 4 Experimental zinc pH adsorption edges at various zinc and carbon concentrations. (a) TLM calibration results for bidentate stoichiometry. (b) TLM calibration results for fractional stoichiometry.



(a) (b)

FIG. 5 Zinc TLM prediction results at high carbon concentrations: (a) bidentate surface species; (b) overall surface species with fractional stoichiometry.

The efficiency in metal removal is affected by the initial metal concentration, with decreasing removal percentages with increasing concentration at constant pH. The pH-removal curves are shifted to more alkaline regions, as previously reported (6–9, 17). This effect has been attributed to surface binding of the low-affinity surface sites as the high-affinity ones begin to reach saturation, causing a reduction of removal efficiency.

The adsorption-pH edges are shifted to more acidic regions with an increase in the carbon concentration. Such an improvement in metal removal can be attributed to an increase in availability of the high-affinity surface sites with an increase in the carbon concentration.

Modeling

Experimental data were used to determine TLM parameters for the single adsorption of Cd and Zn onto Scharlau Ca 346 activated carbon. The TLM describes the adsorption reactions as chemical complexation reactions, but including a coulombic correction factor which accounts for electrostatic interactions between the ionic adsorbate and the surface of the adsorbent. Thus, a surface complexation equilibrium constant is defined by a mass law action corrected by an electrostatic factor. The adsorption process involves several metal–hydroxo surface species adsorbed onto a nonhomogeneous surface characterized by a continuous distribution of surface sites energies (18). Prior to the evaluation of the model constants, the types of surface sites, the number of metal species to be adsorbed, and the stoichiometry of the adsorption reactions must be selected. However, the description of the activated carbon surface and the structure of the metal surface complexes is not yet well defined, because it currently remains an area of research. In this work a simplified surface complexation model, including a unique metal surface reaction, has been considered. With this approach an overall surface complexation reaction, involving all the metal species that participate in the adsorption process, is assumed. Thus, the TLM constant is defined as

$$K_{ads} = \frac{[(\underline{C}O)_x\text{–}M_y(OH)_{(z-x)}][H^+]^z}{[\underline{C}OH]^x\,[M^{2+}]^y}\exp(-F(z\psi_o - 2y\psi_\beta)/RT) \qquad (6)$$

where $[\underline{C}OH]$ is the concentration of total free surface sites, $[(\underline{C}O)_x$-$M_y(OH)_{(z-x)}]$ is the concentration of the overall surface complex, ψ_o and ψ_β are the electrostatic potentials at the o- and β-planes according to TLM theory, F is the Faraday constant, R is the molar gas constant, and T is the absolute temperature.

The complete model formulation also includes possible aqueous complexation and chemical precipitation reactions, represented by chemical equilibrium constants obtained from the available database (16). Two surface complexation reactions for the adsorbent acid–base behavior, previously characterized by pK_{1a} and pK_{2a}, were also needed.

In this work, two model calibration approaches have been checked, as previously discussed for another activated carbon (9). First, bidentate stoichiometry ($x = 2, y = 1, z = 2$) was selected, and the TLM constants for Cd and Zn adsorption were calculated point to point from the experimental data. With this approach the process is represented through a single surface species. Second, the multiple surface metal–carbon interactions were represented through the definition of an overall surface species including fractional stoichiometric coefficients, representing the contributions of the model components (metal, adsorbent, and proton) to the global adsorption process. In this case the stoichiometric coefficients and the TLM constant values were fitted by using an optimization technique.

TLM Calibration for Bidentate Stoichiometry

The model calibration was performed point to point for the data series of carbon concentrations of 5, 10, and 20 g/L. The chemical equilibrium code

MINTEQA2 (16), which solves the nonlinear equations defining the equilibrium problem including adsorption processes, was used. The experimental data series corresponding to Zn adsorption at carbon concentrations of 40 and 100 g/L was used as test data to check the model capacity to reproduce the adsorption behavior out of the calibration range, which finally will be needed to use the model as a prediction tool in continuous column studies.

For both metals the calculated constants showed pH, metal, and carbon concentration dependencies. These dependencies of the constant could be explained on the basis of the assumption of a unique adsorption reaction with bidentate stoichiometry to represent the multiple interactions that occur on the surface of the adsorbent.

The pH, metal, and carbon concentrations dependencies of log K_{ads} were studied, and the resulting expression for log K_{ads} was

$$\log K_{ads} = a + b\cdot\text{pH} + c\cdot\log TM + d\cdot\log C_{carb} \tag{7}$$

where TM represents the total initial metal molar concentration, C_{carb} represents the activated carbon mass concentration, and a, b, c, and d are adjustable parameters.

The adjusted values of the four parameters in Eq. (7) are shown in Table 1 along with the experimental pH, metal, and carbon concentrations ranges. Predicted results obtained with the constants in Table 1 are shown in Figs. 3(a) and 4(a). A good correlation was obtained with mean absolute deviations between experimental and calculated removal percentages of 3.3 for Cd and 3.9 for Zn.

TLM Calibration for Fractional Stoichiometry

In this second alternative, which avoids the observed dependencies of the TLM constant on pH, metal, and carbon concentrations, a different model cal-

TABLE 1

Log K_{ads} for the TLM Bidentate Stoichiometry Single Adsorption of Cadmium and Zinc onto Scharlau Ca 346 Activated Carbon at 20°C: $\log K_{ads} = a + b\cdot\text{pH} + c\cdot\log TM + d\cdot\log C_{carb}$

	Cadmium	Zinc
a	−0.7046	−2.3209
b	−1.5342	−1.4252
c	−0.4216	−0.6485
d	−0.6435	−0.6402
pH range	4–8	4–8
Initial metal concentration range (M)	2×10^{-5}–8×10^{-4}	2×10^{-5}–7×10^{-4}
Carbon concentration range (g/L)	5–20	5–20

TABLE 2

Log K_{ads} and Stoichiometric Coefficients for the Single Adsorption of Cadmium and Zinc onto Scharlau Ca 346 Activated Carbon at 20°C: Adsorbed species $[(\underline{C}O)_x\text{–}M_y(OH)_{(z-x)}]$

	Cadmium	Zinc
Log K_{ads}	−0.638	−2.082
x	2.068	1.401
y	0.597	0.451
z	0.436	0.374
pH range	4–8	4–8
Initial metal concentration range (M)	2×10^{-5}–8×10^{-4}	2×10^{-5}–7×10^{-4}
Carbon concentration range (g/L)	5–20	5–20

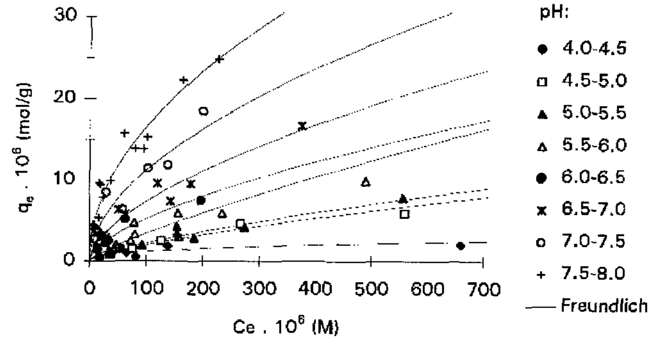
ibration was performed. A unique adsorption reaction with fractional stoichiometry was assumed, and the equilibrium constant value was optimized along with the set of stoichiometric coefficients. This procedure involves the determination of four TLM parameters, the same number as in the bidentate stoichiometry approach. A Rosenbrook optimization (19) technique was implemented in the chemical equilibrium code MINTEQA2, and an experimental data series with carbon concentrations of 5, 10 and 20 g/L was simultaneously used.

The adjusted values of the four parameters, log K_{ads} and the x, y, and z stoichiometric coefficients in Eq. (6), are shown in Table 2 along with the experimental pH, metal, and carbon concentrations ranges. Mean absolute deviations between experimental and predicted removal percentages were 7.7 for Cd and 4.7 for Zn.

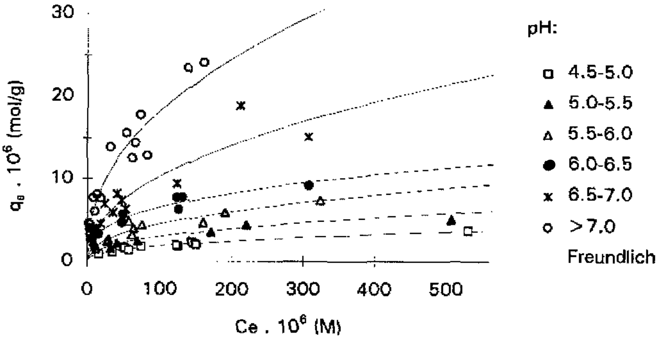
Comparison of the results obtained for the two calibration procedures shows that different predictions in the experimental calibration range of 5 to 20 g/L of activated carbon can be achieved with both models. This result points out how the selection of the simplified approach in the TLM calibration stage can affect the model prediction capacity.

TLM Simulation Results

Once the TLM parameters were determined for the two tested model approaches, simulations of Zn adsorption at activated carbon concentrations of 40 and 100 g/L were performed, and the results are shown in Fig. 5. Inspection of the figure corroborates that the model responses are quite different. Model predictions corresponding to simulations with the bidentate stoichiometry were closer to the experimental data than the predictions obtained with the fractional stoichiometry model. Although both models showed acceptable predictions in the calibration stage with a wide carbon concentration range for batch experiments, the discrepancy obtained in the simulation of the adsorption behavior for severe experimental conditions (high carbon concentration data series) confirms the importance of the model fit process in the subsequent applicability to column studies. Mean absolute deviations between experimental and simulated removal percentages were 4.9 for the bidentate stoichiometry and 6.6 for the fractional stoichiometry. Therefore, the model based on the bidentate stoichiometry with a K_{ads} dependent on pH, metal, and carbon concentrations has been shown as the best alternative to be used at high carbon concentrations for the system Zn–Scharlau Ca 346. These conclusions



(a) Cadmium



(b) Zinc

FIG. 6 Adsorption isotherms: (a) cadmium; (b) zinc.

TABLE 3
Freundlich Isotherm for Cadmium and Zinc onto Activated Carbon Scharlau Ca 346

Cadmium				Zinc			
pH	K_F (L/g)	n	r^2	pH	K_F (L/g)	n	r^2
4.0–4.5	4.34×10^{-5}	1.532	0.864				
4.5–5.0	1.44×10^{-3}	1.396	0.959	4.5–5.0	7.98×10^{-5}	2.451	0.954
5.0–5.5	1.73×10^{-3}	1.381	0.960	5.0–5.5	1.33×10^{-3}	2.429	0.954
5.5–6.0	5.58×10^{-3}	1.245	0.920	5.5–6.0	2.11×10^{-4}	2.394	0.916
6.0–6.5	1.54×10^{-3}	1.619	0.966	6.0–6.5	1.54×10^{-4}	2.914	0.950
6.5–7.0	1.79×10^{-3}	1.677	0.942	6.5–7.0	7.03×10^{-4}	2.178	0.903
7.0–7.5	1.63×10^{-3}	1.850	0.912	>7.0	1.01×10^{-4}	2.289	0.922
7.5–8.0	1.60×10^{-3}	2.015	0.927				

are in agreement with those previously obtained for the adsorption of Cd and Cu onto activated carbon Darco 12–20 mesh (9).

Adsorption Isotherms

The experimental data can also be shown as adsorption equilibrium isotherms at constant pH. For this purpose, single metal data of the series with carbon concentrations of 5, 10, and 20 g/L have been grouped in several isotherms through the experimental pH range, each one corresponding to 0.5 pH unit interval. Such a representation is shown in Fig. 6 as plots of a solid-phase equilibrium metal concentration (q_e), expressed as mol metal per gram sorbent, versus the liquid-phase equilibrium metal ion concentration (C_e), expressed as molar concentration. The adsorption isotherms exhibit non-Langmuir behavior, which indicates a nonmonolayer adsorption. Data were mathematically modeled by the Freundlich adsorption isotherm:

$$q_e = K_F C_e^{1/n} \tag{8}$$

The isotherm parameters obtained by linear regression are presented in Table 3. Although experimental data were correlated with the Freundlich equation, estimation of removal percentages resulted in greater mean absolute deviations (5.4 for Cd and 6.6 for Zn) than TLM predictions. Correlation of the isotherm parameters with pH were not found, so the applicability of the Freundlich model to the prediction of the adsorption in the Cd–Scharlau Ca 346 and Zn–Scharlau Ca 346 systems in the whole pH range should require the conjunctive use of one equation for each pH. Furthermore, even Freundlich predictions of removals at higher carbon concentrations (40 and 100 g/L) were unacceptable, corroborating the limitations of the adsorption isotherm.

CONCLUSIONS

Scharlau Ca 346 granular activated carbon is able to remove Cd and Zn from aqueous solutions. The adsorption in these systems depends on the solution pH, the initial metal concentration, and the carbon dose at constant temperature. Increases in pH and carbon concentration yield greater removal efficiency, while increases of the initial metal concentration reduce the metal removal percentages. Single Cd and Zn adsorption SCF modeling was carried out by assuming the simplest surface complexation reactions with two alternative models: a single surface bidentate species and an overall surface species including a fractional stoichiometry. The bidentate stoichiometry model successfully predicted experimental pH–removal curves for the single adsorption of Cd and Zn in the complete experimental carbon concentration range, so the model should be adequate for column system application. The Freundlich adsorption isotherm was also tested and showed limitations when compared with TLM in a wide range of pH and carbon concentration conditions.

ACKNOWLEDGMENT

This study was supported by Generalitat Valenciana (Grant GV-2233/94).

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Received by editor April 17, 1998
Revision received September 1998