Modeling of heavy metals removal from aqueous solution using activated carbon produced from cotton stalk

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ABSTRACT

Activated carbon produced from cotton stalks was examined for the removal of heavy metal contaminants. Adsorption studies in completely mixed batch reactors were used to generate equilibrium pH adsorption edges. Continuous flow experiments using the activated carbon in fixed beds were conducted to determine heavy metal breakthrough versus bed volumes treated. At given pH value in the range 5–7, the adsorption capacity was similar for copper and lead and clearly greater than for cadmium. A surface titration experiment indicated negative surface charge of the activated carbon at pH > 6, meaning that electrostatic attraction of the divalent heavy metals can occur below the pH required for precipitation. Substantive metal removal below the pH of zero charge might be due to surface complexation. Accordingly, a surface complexation model approach that utilizes an electrostatic term in the double-layer description was used to estimate equilibrium constants for the protolysis interactions of the activated carbon surface as well as equilibria between background ions used to establish ionic strength and the sorbent surface. Pb(II) adsorption edges were best modeled using inner-layer surface complexation of Pb\(^{2+}\), while Cd(II) and Cu(II) data were best fit by outer-layer complexes with Me\(^{2+}\). The full set of equilibrium constants were used as input in a dual-rate dynamic model to simulate the breakthrough curves of the target metals (Pb, Cu and Cd) from fixed bed experiments and to estimate external (or film) diffusion and internal (surface) diffusion coefficients.

Key words | activated carbon, adsorption equilibria, cotton stalks, heavy metals, modeling

INTRODUCTION

Numerous studies have been conducted for removal of heavy metals from waters and wastewaters. Ion exchange, reverse osmosis, and chemical precipitation have been investigated extensively (Dabrowski et al. 2004; Fu & Wang 2011; Grimshaw et al. 2011), but they are often costly, as in the case of reverse osmosis, or incapable of meeting treatment objectives, as in chemical precipitation. Adsorption has been proved to be a potentially feasible alternative (Mohan & Gandhimathi 2009). Adsorption by using activated carbon is the most common method, but this too may be expensive, particularly if proper raw materials are not available, requiring the carbon to be imported (Zaini et al. 2010). Motivated by cost considerations, locally generated agricultural wastes such as cotton stalks, rice straw, sugar cane bagasse, and others have been tested in the production of activated carbon in developing countries (Kadirvelu et al. 2001; Logan & Yevich 2002). This research investigated the effectiveness of activated carbon produced from cotton stalks in the adsorption of three target heavy metals – lead, cadmium, and copper – from aqueous solution.

Surface complexation models have been used to describe and interpret metal ion adsorption equilibria. Flow through treatment systems, in particular fixed beds, are the most efficient mode for porous adsorbents such as activated carbon (Di Natale et al. 2009). Effective modeling of the behavior and performance of fixed bed adsorbers requires a dual-resistance mass transfer approach that considers external (film) and internal (surface) diffusion of the sorbate with respect to carbon particles (Vaughan et al. 2007). Models of this type have seldom been implemented for metal adsorption due to the challenge of incorporating surface complexation equilibrium relationships into the solution of the solid phase and the liquid phase mass balances.
comprising the dynamic model (Smith 1998). In this study
the triple-layer surface complexation model (TL-SCM) was
used for the determination of sorbent surface equilibrium
constants from potentiometric titration data. These values
were then used to estimate adsorption equilibrium constants
from pH adsorption edge data for the three target heavy
metals: lead, cadmium, and copper. Finally, the full set of
equilibrium constants were then used as input in a dual-rate
dynamic model to simulate the breakthrough curves
of the target metals from fixed bed experiments. The ultimate
objective of these studies is to use the model as a
scale-up tool for design of either pilot- or full-scale units con-
taining locally produced activated carbon. Verification of a
modeling tool to simulate performance and facilitate
design for adsorption units with activated carbon produced
from agricultural waste is an important contribution to the
literature and to engineering practice pertaining to the
advanced treatment of heavy metals in wastewater.

MATERIALS AND METHODS

Activated carbon

The activated carbon used in this work was produced from
cotton stalks, with the production procedure and carbon
properties described in a previous work (Girgis et al. 2009).
The carbon had a surface area of ~740 m²/g compared to
commercial activated carbons, which vary from 500 to
1,800 m²/g. For this research, a sample of the produced
carbon was sieved using US standard sieves. The pass 200
mesh fraction was used for the surface titration experiment,
and 35–50 mesh fraction was used in the adsorption exper-
iments. A primary objective of using activated carbon
produced from cotton stalks is to address a major solid
waste management problem in Egypt, namely the disposal
of agricultural wastes. Approximately 25 million tons are
produced per year with 1.5–2 tons/year being cotton stalks.
These wastes are most often burnt in open fields or in primit-
ive ovens, releasing considerable amounts of toxic and
greenhouse gases to the atmosphere every harvest season,
threatening the health of millions in the Nile River valley
(Louis 2006). Therefore, conversion of large quantities of
organic wastes into activated carbon would aid in addressing
a severe air pollution problem in addition to producing a
marketable and environmentally useful product. Continuous
flow column studies showed a good affinity of the produced
activated carbon for the target heavy metals compared to
compared the cost of producing activated carbon from Egyp-
tian cotton stalks with commercial carbons, and determined
that the cost of the imported activated carbon exceeds a
locally produced adsorbent by approximately three times.
Moreover, local production can promote economic benefits
such as creating local job opportunities and earning foreign
exchange.

Surface titration

Surface charge characteristics were estimated using poten-
tiometric titration. A 0.5 g dry sample (200 × 325 mesh)
was titrated in a Teflon reaction vessel containing 50 mL
of deionized distilled water at room temperature to yield a
solid concentration of 10 g/L. The suspension was continu-
ously stirred and purged by ultra-pure nitrogen gas prior to
titration in order to remove CO₂ that would interfere with
an acid–base titration. NaNO₃ was used as an ionic back-
ground in order to standardize the solution. Standard
0.1 M NaOH was incrementally added to the suspended sol-
ution to raise the pH, and standard 0.1 M HNO₃ was
incrementally added to lower the pH. The pH was measured
for increments of 0.1 mL for both acid and base. The exper-
iment was done for ionic backgrounds of 0.1, 0.01, and
0.001 M to examine the impact of background total dis-
solved solids concentration on surface charge of the carbon.

Batch equilibrium experiments

All the synthetic solutions had the same molar concen-
tration of metal of ~48 μM. This corresponds to Pb, Cd,
and Cu concentrations of 10.0, 5.4, and 3.1 mg/L, respect-
ively – concentrations within a typical range of what may
be encountered in industrial wastewaters (Smith & Amini
2000). The same molarity was used so that the relative
adsorption capacity of the target metals could be compared
in a meaningful way. The purposes of this set of experiments
were to determine the pH adsorption edge for the three
target heavy metals and the impact of system variables on
adsorption capacity. The target equilibrium pH range was
3–11. A reaction time of 72 hours was used, as batch rate
studies demonstrated this as sufficient for attainment of
equilibrium for the designated carbon particle size. Three
experiments were conducted for each target metal: (1) no
sorbent – to determine metal precipitation as a function of
pH; (2) carbon dose of 0.5 g/L; and (3) carbon dose of
1.0 g/L. NaNO₃ (at 0.01 M) was used as the ionic back-
ground in order to standardize the solution. Metal
concentrations were determined using a SIMAA 6000
(Perkin Elmer) atomic absorption (AA) spectrophotometer with transversely heated graphite furnace and Zeeman coloration. All samples were diluted to meet the reading range of the AA device (0–200 ppb).

Column experiments

This set of experiments was conducted using stainless steel columns of internal diameter 7 and 80 mm length for all experiments. The solutions were administered to the column by a positive displacement pump that delivered the solution from a polypropylene container (with a tight cover) to the bottom of the column. At the bottom of the column there is a three-way valve that directs the influent either to the column or to waste/sampling. For each experiment with the three target metals (Pb, Cd, Cu), a carbon bed was placed in all of the columns and the influent pH was 5.5; and the influent metal concentration was ~48 μM.

Surface complexation modeling

Of the various surface complexation models used to represent adsorption equilibria of metals, the triple-layer model (TLM) offers the advantage of accounting for ionic strength effects on aqueous–surface interactions (Chen & Lin 2004) in addition to both chemical and electrostatic interactions with ionic aqueous species by providing a more complete depiction of the electrical double-layer (Davis & Kent 1990). The TLM can consider inner-layer (α-plane) and outer-layer (β-plane) surface complexes with adsorbable and electrolyte species in addition to diffuse layer interactions as in conventional double-layer theory (Schindler & Stumm 1987). Mathematical depiction of the TLM includes mass balances, charge balances, and surface equilibrium equations. Mass balances for the electrolyte species, assuming NaNO₃ background as in work, are:

\[ C_{T, \text{NO}_3} = [\text{NO}_3^-] + [>\text{SOH}_2^+ - \text{NO}_3^-] \]  (1)

\[ C_{T, \text{Na}^+} = [\text{Na}^+] + [>\text{SO}^- - \text{Na}^+] \]  (2)

The surface site balance, considering an inner-layer, undentate surface complex for an adsorbed divalent metal species, Me²⁺, is:

\[ C_{T, \text{SO}^-} = [>\text{SOH}_2^+] + [>\text{SOH}] + [>\text{SO}^-] + [>\text{SO}^- - \text{Na}^+] \]
\[ + [>\text{SOH}_2^- - \text{NO}_3^-] + [>\text{SOMe}^+] \]  (3)

The total soluble Me(II) mass balance for the equilibrium condition is:

\[ C_{T, \text{Me(II)(sol)}} = [\text{Me}^{2+}] + [\text{MeOH}^+] + [\text{Me(OH)}_2^0] \]
\[ + [\text{Me(OH)}_3^-] + \ldots \]  (4)

The inner-layer charge balance equates total adsorbed concentrations in the inner layer with the total charges in the α-plane. Again for the assumption of inner-layer adsorbed complex, this is:

\[ [>\text{SOH}_2^+] + [>\text{SOH}_2^- - \text{NO}_3^-] + [>\text{SOMe}^+] \]
\[ - [>\text{SO}^-] - [>\text{SO}^- - \text{Na}^+] = \frac{S_C S_A}{F} (\psi_o - \psi_\beta) \]  (5)

where \( S_C \) is the concentration of solid (g/L), \( S_A \) is surface area of the adsorbent, \( F \) = Faraday constant (coulombs/mole), \( C_1 \) is inner-layer capacitance (F/m²), and \( \psi \) is the average electrostatic potential (volt) at the α- and β-plane, respectively (Schindler & Stumm 1987; Sreejalekshmi et al. 2009). The analogous outer-layer charge balance is:

\[ [>\text{SO}^- - \text{Na}^+] - [>\text{SOH}_2^- - \text{NO}_3^-] \]
\[ = \frac{S_C S_A}{F} [C_1(\psi_\beta - \psi_o) + C_2(\psi_\beta - \psi_d)] \]  (6)

where \( C_2 \) is outer-layer capacitance (F/m²), and \( \psi_d \) is the average electrostatic potential (volt) in the diffuse layer. Finally, the charge balance for the diffuse layer is:

\[ C_2(\psi_d - \psi_\beta) = 0.1174\sqrt{I} \sinh \left( \frac{F\psi_d}{2RT} \right) \]  (7)

where \( R \) = universal gas constant (cal/K-mole), \( T \) = absolute temperature (K), and \( I \) = ionic strength (mol/L) (Smith 1998).

The relevant equilibria include the metal-hydrolysis mass law expressions according to:

\[ K_{n, \text{hydrolysis}} = \frac{[\text{Me(OH)}_{2-n}^n][\text{H}^+]}{[\text{Me}^{2+n}]} \]  (8)

The two protolysis equilibria for the three surface species (Equations (11) and (12)), two expressions
representing background electrolyte interactions with the surface species (Equations (13) and (14)), and two adsorption equilibria representing potential inner- and outer-sphere surface complexes (Equations (15) and (16)) are given in the following section where they can be presented with their corresponding data and values. The nonlinear systems of Equations (1)–(8) and (11)–(16) were solved using a Newton–Raphson algorithm that is described in detail in Smith (1998).

RESULTS AND DISCUSSION

Adsorption equilibria and modeling

Metal ion adsorption from solution is assumed to occur at functional group sites on the surface of activated carbon. The predominant adsorption sites for this case are assumed to be >SOH₂⁺, >SOH, and >SO⁻. The following protolysis reactions describe the acid-base chemistry of the surface:

\[
>\text{SOH} + \text{H}^+ \leftrightarrow >\text{SOH}_2^+ \\
>\text{SOH} \leftrightarrow >\text{SO}^- + \text{H}^+ 
\]

in which the surface species >SOH₂⁺, >SOH, and >SO⁻ can acquire and/or give up protons in solution. TL-SCM expressions for the equilibrium constants of reactions (1) and (2), respectively, are:

\[
K_{S1} = \frac{[>\text{SOH}_2^+]}{[>\text{SOH}][\text{H}^+]} \exp \left( \frac{F\psi_o}{RT} \right) 
\]

\[
K_{S2} = \frac{[>\text{SO}^-][\text{H}^+]}{[>\text{SOH}]} \exp \left( - \frac{F\psi_o}{RT} \right) 
\]

where \( K_{S1} \) and \( K_{S2} \) are equilibrium constants for the respective surface protolysis reactions, and \( F, R, T, \) and \( \psi_o \) are as defined previously (Schindler & Stumm 1987; Sreejalekshmi et al. 2009). Interactions of electrolyte ions with the surface species are assumed to be weaker outer-sphere complexes according to the following reactions with corresponding equilibrium expressions.

\[
>\text{SOH} + \text{H}^+ + \text{NO}_3^- \leftrightarrow (>\text{SOH}_2^- - \text{NO}_3^-) 
\]

\[
K_{E1} = \frac{[>\text{SOH}_2^- - \text{NO}_3^-]}{[>\text{SOH}][\text{H}^+] [\text{NO}_3^-]} \exp \left( - \frac{F(\psi_\beta - \psi_o)}{RT} \right) 
\]

\[
>\text{SOH} + \text{Na}^+ \leftrightarrow (>\text{SO}^- + \text{Na}^+) + \text{H}^+ 
\]

\[
K_{E2} = \frac{[>\text{SO}^- + \text{Na}^+][\text{H}^+]}{[>\text{SOH}][\text{Na}^+]} \exp \left( - \frac{F(\psi_\beta - \psi_o)}{RT} \right) 
\]

where \( \psi_o \) is the average potential (volt) of the outer, or \( \beta \), plane. Model calculations also required the surface area of the sorbent (m²/g), surface site density (sites/nm²) and linear charge potential (F/m²). A nonlinear, least squares optimization package, FITEQL (Herbelin & Westall 1994), was used to estimate the equilibrium constants \( K_{S1}, K_{S2}, K_{E1}, \) and \( K_{E2} \) from titration data according to a calibration procedure described previously (Smith 1998). The plot of titration data at two ionic strengths together with TL-SCM simulations is given in Figure 1. The log \( K_i \) values are:

\[
\log K_{S1} = 2.70 \quad \log K_{S2} = -4.80 \quad \log K_{E1} = 5.90 \quad \log K_{E2} = -9.00
\]

and the pH point of zero charge (pH\(_{pzc}\)) is ~5.6. Although changing one or more constants may slightly improve the model fit of a given data set, the objective was to obtain a single set of ‘constants’ that capture the effects of variation in background ionic strength. For instance, the set of \( K_i \) values above yielded a sum of squares of the errors (SSE) between model versus data pH values of 3.14 and 6.87 for 0.01 and 0.001 M ionic strength titrations, respectively. The error is calculated in this fashion since pH is the dependent variable deriving from a given volume of acid or base added. The combined error of 10.01 was the

Figure 1 | Potentiometric titration data and TL-SCM simulations for activated carbon.
minimum of any set of $K_i$ trials for the two ionic strengths tested.

For heavy metals adsorption, an understanding of the aqueous chemistry of a given system is required in order to estimate the appropriate sorbate–surface interactions. In particular, the hydrolysis and precipitation of Me(II) hydroxides needs to be included in the analysis. Significant Pb(OH)$_2$ precipitation occurs at pH as low as 6–7, while for Cd(OH)$_2$ it will be pH 9–10 and Cu(OH)$_2$ is at pH 7–8. Therefore, the sorption mechanism is most obvious at pH values less than values at which Me(II) precipitation is evident. For all three target metals, the predominant aqueous species is Me$^{2+}$ at these lower pH values. Therefore, the most likely adsorption reactions used in the TLM-SCM of adsorption equilibria were inner- and outer-layer complexes of Me$^{2+}$ according to the following.

Inner Layer: \[ \text{SOH} + \text{Me}^{2+} \rightleftharpoons \text{SOMe}^+ + \text{H}^+ \]

\[ K_{\text{ads,1}} = \frac{[> \text{SOMe}^+][\text{H}^+]}{[> \text{SOH}][\text{Me}^{2+}]} \exp \left( F\phi_0/RT \right) \quad (15) \]

Outer Layer: \[ \text{SOH} + \text{Me}^{2+} \rightleftharpoons (>\text{SO}^- - \text{Me}^{2+})^+ + \text{H}^+ \]

\[ K_{\text{ads,2}} = \frac{[ (> \text{SO}^- - \text{Me}^{2+})^+][\text{H}^+]}{[> \text{SOH}][\text{Me}^{2+}]} \exp [-F(\phi_0 - 2\phi_0)/RT] \quad (16) \]

Batch equilibrium pH adsorption edges are presented in Figures 2–4 for Pb, Cd, and Cu, respectively. Data are presented for carbon doses of 0.5 and 1.0 g/L. The dashed curve (with associated precipitation data) in each figure represents the model calculation for Me-hydroxide precipitation only and target initial Me(II) concentration; i.e., no carbon present. The solubility product used in model calculations was obtained by model calibration of laboratory data for a concentration of 48 μM for each target metal. Figures 2–4 indicate that substantial adsorption occurred at pH values well before the onset of precipitation. Using the log $K_{\text{Si}}$ and log $K_{\text{Ei}}$ constants for the surface in NaNO$_3$ electrolyte, the adsorption equilibrium constants were determined from model calibration of the pH adsorption edge data. Pb(II) equilibria were best simulated by an inner-layer complex of Pb$^{2+}$ (Equation (15)), while Cd(II) and Cu(II) were best fit using an outer-layer complex with Cd$^{2+}$ and Cu$^{2+}$, respectively. Adsorption equilibrium constants as well as those for metal hydrolysis and metal-hydroxide precipitation used in model calculations are listed in Table 1.

As in the case of $K_{\text{Si}}$ and $K_{\text{Ei}}$, the objective was to obtain a single adsorption equilibrium constant for a given metal that captured the effects of variable sorbent dose. The parameter search minimized the net error in the percent removal between experimental values and model calculations for a given value of pH (the independent variable) for both dosage cases together, taking into account errors in either direction; i.e., errors could be positive or negative.
which is consistent with the electronegativity of these metals; namely, 1.85, 1.854, and 1.52 respectively.

### Modeling of dynamic systems

Breakthrough curves for fixed bed activated carbon columns are presented in Figures 5–7 for Pb, Cd, and Cu, respectively. Breakthrough is rapid in every case because of the low empty bed contact time (EBCT) employed. The principal objective here was to demonstrate the use of the TL-SCM equations and constants to perform the equilibrium calculations needed to execute dual-rate dynamic model simulations (Limousin et al. 2007). A homogeneous surface diffusion description of intraparticle transport that includes film diffusion from bulk solution to the carbon surface was used. The liquid- and solid-phase mass balance equations assume spherical carbon particles and negligible axial dispersion and are, respectively:

\[
\frac{\partial C_z}{\partial t} = -v_z \frac{\partial C_z}{\partial z} - \rho \frac{1 - \varepsilon}{\varepsilon} \frac{\partial Q_{avg,z,t}}{\partial t}
\]

Figure 5 | Column data and model simulation for Pb(II) adsorption onto activated carbon.

Figure 6 | Column data and model simulation for Cd(II) adsorption onto activated carbon.
The solid-phase boundary condition at the particle surface

\[ C = \text{liquid-phase concentration}, \quad Q = \text{sorbent-phase} \]

\[ k_i(C_L - C_S) = \rho D_i \frac{\partial Q_{R_{i,j}}}{\partial r} \]  

(19)

where \( C_S = \text{liquid-phase concentration at the particle surface} \), and \( R = \text{sorbent radius} \). The equations together with boundary and initial conditions and TL-SCM equilibrium equations were solved using a method described previously (Smith 1998). Best fit simulations yielded kinetic coefficients presented in Table 2 for the target metals. The search is performed by calibration of the dynamic model for a data set using the previously and independently determined equilibrium parameters for a given metal. The incipient breakthrough of solute in the column effluent enables accurate estimation of \( k_i \) from this initial portion. A nonlinear regression analysis is then used to search for the value of \( D_i \) over the remaining portion of the data profile. A minimization function based on the square of the residuals is used for both parameter searches, where the residual is the difference between the dimensionless model and experimental concentrations of soluble metal in the column effluent at a given time. The minimization parameter, \( R_{\text{min}} \), is given in Table 2 for the best-fit search for each metal. To give an idea of the sensitivity in the kinetic parameter search, for the same \( k_i \) but altered \( D_i \) value of \( 2.0 \times 10^{-11} \text{ cm}^2/\text{s} \) for Pb, the \( R_{\text{min}} \) increases to 0.1822 or double the best-fit value for \( D_i \) of \( 4.5 \times 10^{-11} \text{ cm}^2/\text{s} \).

While the dynamic model in its current stage of development is not fully robust in that it does not automatically compute breakthrough curves for time-variable changes in influent pH, Figures 6 and 7 indicate that it can predict fixed bed performance for time variations in influent metal concentration as given by the fine dotted ‘influent’ line in Figures 5–7. The model can also handle changes in ionic strength of the influent provided the value is within the range of ionic strength concentrations for which a consistent set of TLM hydrolysis constants were evaluated for the sorbent, in this case the 10-fold range of \( 10^{-3} – 10^{-2} \text{ M} \).

**CONCLUSIONS**

1. An activated carbon produced from cotton stalks exhibited potential to adsorb heavy metals, even at pH values less than the pH\(_{\text{zpc}} \), demonstrating that metal removal is a result of surface complexation in addition to electrostatic interactions as with other heavy metal sorbents (Vaughan & Reed 2005). At pH values approaching neutral and above, co-precipitation will also probably have some impact, especially for Pb and Cu which exhibit lower solubility (Smith & Amini 2000).

2. Potentiometric titration showed that the surface charge density of the produced activated carbon decreased with an increase in pH, similar to other activated carbons with high cationic heavy metal adsorption capacity (Chen & Lin 2001). Consistent with this characteristic, the pH adsorption edges exhibited higher percentage removal with increasing pH.

3. A TL-SCM was used to describe surface protonation of the activated carbon at various ionic strengths assuming >SOH\(_2\), >SOH, and >SO\(_{-}\) surface species, and the equilibrium relationship of Me(II) adsorption as a function of pH and carbon dose. Pb(II) adsorption edges were best modeled using inner-layer surface complexation of Pb\(^{2+}\), while Cd(II) and Cu(II) data were best fit by outer-layer complexes with Me\(^{2+}\). Metal removal capacities by the carbon were in the order Cu \( \approx \) Pb > Cd which is consistent with the electronegativity of these metals of 1.85, 1.854,
and 1.52 respectively. Other investigators have reported high Cu removal efficiency relative to other metals such as zinc and cobalt (Chen & Lin 2001), and high adsorption of Pb relative to Cd (Smith 1998).

4. Dynamic performance of metal adsorption in fixed beds was simulated using a homogeneous surface diffusion model with TL-SCM calculations to describe the equilibrium relationship at the particle surface at each bed/time step. Breakthrough was rapid in every case because of the low EBCT employed and more sensitive to equilibrium than kinetic parameters (Smith & Amini 2000; Vaughan et al. 2007). Moreover, it was found that controlling the pH in the kinetic experiments does not significantly affect the adsorption equilibrium (Chen & Lin 2001; Limousin et al. 2007). Finally, while carbon loading of heavy metals at breakthrough and exhaustion compare favorably with commercial activated carbons, the values are less than those obtained for artificially modified activated carbons and oxide adsorbents (Reed et al. 1996; Smith & Amini 2000; Chen & Lin 2004).

REFERENCES


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