REMOVAL OF HEAVY METALS FROM SOLUTION BY A NOVEL SWINE MANURE-BASED ACTIVATED CARBON

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SUMMARY: Pelletized swine manure was pyrolyzed and steam-activated at various activation times (from 15 to 60 min) and water flow rates (1, 3 and 5 ml/min) to produce granular activated carbons. The adsorption behavior of these carbons towards four different metals (Cu\(^{2+}\), Cd\(^{2+}\), Ni\(^{2+}\) and Zn\(^{2+}\)) at 5 mM concentrations was measured individually and in competition mode. The ability of the swine manure-based carbons, SMC to adsorb the metal ions was compared with that from carbons made from three traditional precursors, coal, coconut and wood. The activation strategy had an influence on the carbon’s ability to adsorb the metals, both individually and in competition. Activated carbons were most effective at adsorbing copper ions and zinc ions with adsorption values ranging respectively between 66.8 % to 91.8% and 39.7 to 77.0% of total metal ion available. These values were significantly larger than the ones found for coal-, coconut shells- and wood-based carbons, with adsorption values of 0%, 24.9% and 23.0% for copper ion and 7.3%, 6.0% and 14.8% for zinc ion, respectively. Adsorption of each metal ion decreased when all metal ions were present and the highest removal rate observed was obtained for 30 min activation at 3ml/min flow rate, with 54.3%, 18.9% and 18.1% for copper, cadmium and zinc ions, respectively. The kinetics of copper ion adsorption were investigated using four different models: a pseudo first-order, a pseudo second-order, the Elovich model and the intraparticle diffusion model. The intraparticle diffusion and Elovich models were good representations of the adsorption kinetics of copper ion by the swine manure-based carbon, with the Elovich equation giving the best fit for the experimental data. It is believed that the conversion of over abundant and worldwide environmentally-problematic swine manure to activated carbon for heavy metals remediation could represent a novel approach to animal waste utilization.

1. INTRODUCTION

The impact of excessive animal manure production on the quality of life and the environment is generating public and regulatory concern. Additionally, water quality issues and the dwindling availability of potable water have become a hot topic worldwide. Viable value-added alternatives that involve the reuse, rather than disposal of animal manures, are therefore in need. Activated carbons, usually made by pyrolysis and activation of either decomposed plant material such as coal, or plant feedstock such as coconut hulls and wood, can also be produced from innovative sources such as animal manures. Chars can be either steam-activated or chemically-
activated, depending on the application and the feedstock. Generally speaking, commercial plant-based carbons while excellent at adsorbing various organic constituents from air or water, have limited ability to remove metals, unless they undergo chemical activation, necessary to confer either a positive or negative charge to the carbon.

Several reports have been published in the literature looking into making activated carbons from less traditional feedstock such as agricultural and municipal wastes. Advantages of using these alternate materials as carbon precursors include being readily available, renewable and cheaper. The removal of heavy metals by carbons prepared using a number of feedstock such as fruit stones (Ferro-Garcia, M.A., Rivera-Utrilla, J. & al, 1988; Perez-Candela, M., Martin-Martinez, J.M. & al, 1995), nut shells (Chamarthy, S., Seo, C.W. & al, 2001; Dastgheib, S.A. & Rockstraw, D.A. 2001), legume hulls (Periasamy, K. & Namasivayam, C. 1994), corn cobs (Vaughan, T., Seo, C.W. & al, 2001), and municipal sludge (Fitzmorris, K.B., Lima, I.M. & al, 2006) has been reported in the literature. Existing research into the use of animal manure as a source for activated carbons is extremely limited, probably because of its lower elemental carbon content and lower yields than plant material. Carbons have been manufactured from chicken litter (Biletiski, B. 1979) and cow manure (Das, D.D., Mahapatra, R. & al, 2000).

Our laboratory at the Southern Regional Research Center in New Orleans, Louisiana, has studied both physical, chemical and adsorptive characteristics of carbons made from poultry manure (Lima, I.M. & Marshall, W.E. 2005a,b,c; Fitzmorris, K.B., Lima, I.M. & al, 2006). More recently swine manure-based carbons were shown to have good capacity towards metal ions such as copper, cadmium and zinc individually (Lima, I.M. and Marshall, W.E., 2007). It is important to extend the investigation to a competitive situation where all species are present at once and to compare them with carbons made from coal, coconut hulls and wood. Additionally, adsorption kinetics experiments with copper ion were conducted and different kinetic models, such as the pseudo first-order and pseudo second-order equations, the intraparticle diffusion model and the Elovich model were used to analyze the adsorption process of copper ion onto the swine manure carbon, that is to describe the rate and the mechanism of adsorption and to determine the factors controlling the rate of adsorption.

2. EXPERIMENTAL STUDY

2.1 Percursor Materials

Swine manure was provided by the Swine Unit, Animal Science Department, Louisiana State University, Baton Rouge, LA. Manure was air dried to less than 20% moisture (w.b.) and subsequently milled in a Retsch cross-beater mill (Glen Mills, Clifton, NJ) to less than 1 mm particle size and pelletized in a PMCL5 Lab pellet mill (California Pellet Mill, Merrimack, NH) to produce cylindrical pellets (4.76 mm diameter and approximately 13 mm length). Three reference carbons made from three common precursors for carbon production: coal, coconut shells and wood were prepared the same way. Coal was received from Beury Mountain Carbon (Hico, WV) and coconuts and hardwood were purchased at local stores. One commercial carbon, with enhanced metal ion adsorption ability was studied for comparison purposes: PÜR RF (Replacement Filter) is a coal-based product found in PÜR brand drinking water filtration systems (Recovery Engineering Corp., Minneapolis, MN) that claims removal of lead, organics and chlorine from drinking water.
2.2 Activation method

Pelletized swine manure was placed in a Lindberg bench furnace equipped with a retort (Lindberg/Blue M, Waterton, WI). Pellets were pyrolyzed at 700°C for one hour under a flow of nitrogen gas set at a flow rate of 40 ml/min. The pyrolyzed pellets were then steam activated at 800°C by pumping water via a peristaltic pump into a flow of nitrogen gas entering the heated retort. Different activation conditions were achieved by allowing water to flow at 3 different rates, 1, 3 and 5 ml/min for 15, 30, 45 or 60 min. Activated carbons cooled in the retort to room temperature, overnight. Surface-ash was removed by washing the carbons with 0.1 M HCl and subsequently triple-rinsing to remove excess acid. Carbons were dried overnight in a convection oven at 80°C and ground with a mortar and pestle to specific particle sizes depending on the test.

2.3 Metal adsorption studies

For metal ion uptake studies, buffered metal ion solutions were used to minimize fluctuations in pH and their possible influence in adsorption. Metal ion uptake was determined using the methods of Lima, I.M. and Marshall, W.E. (2005c). For kinetic studies, aliquots were taken at specific time intervals (1, 2, 5, 10 and 30 min, 1, 2, 4 and 24 hr). Copper was the selected metal as it was the metal ion with the highest affinity for the carbon. The rate parameters were determined by experimentation, by fitting data to several published kinetic processes in order to investigate the best representation for the adsorption data. Copper ion adsorption data for the swine manure-based carbons was fitted to four different kinetic models: a pseudo first-order (Lagergren, S. 1898), a pseudo second-order (Ho, Y.S. & McKay, G. 1999), the Elovich equation (Dermibas, E., Kobya, M. & al, 2004; Chien, S.H. & Clayton, W.R., 1980) and the intraparticle diffusion model (Srivastava, S.K., Tyagi, R. & al, 1989, Weber, W.J. & Morris, J.C., 1963).

2.3.1 Pseudo first-order equation

The pseudo first-order adsorption kinetic rate equation can be defined as:

\[
\frac{dq_t}{dt} = k_1 (q_e - q_t)
\]

where \( q \) is the adsorption efficiency, \( q_t \) at time \( t \) and \( q_e \) at equilibrium, in mmol/g and \( k_1 \) is the adsorption rate constant for the pseudo first-order kinetic model, in hr\(^{-1}\). Integrating the above equation between \( t = 0 \) and \( t = t \) and \( q_e = 0 \) and \( q_t = q_t \) yields:

\[
q_t = q_e \left(1 - e^{-k_1t}\right)
\]

The adsorption rate constant \( k_1 \) and the equilibrium adsorption efficiency, \( q_e \) are obtained from a non-linear regression fit (exponential rise to max, single, 2-parameter fit) by using least squares regression implemented by Sigma Plot v.10.0.0.54 for windows 2000 (SPSS Inc. Chicago, IL).

2.3.2 Pseudo second-order equation

The pseudo second-order adsorption kinetic rate equation can be defined as:

\[
\frac{dq_t}{dt} = k_2 (q_e - q_t)^2
\]
where $q$ is the adsorption efficiency, $q_t$ at time $t$ and $q_e$ at equilibrium, in mmoles.g$^{-1}$, and $k_2$ (g.mmoles$^{-1}$.hr$^{-1}$) is the adsorption rate constant for the pseudo second-order kinetic model. For the same boundary conditions as for Equation (1), the resulting integrated equation for the pseudo second-order reaction is:

$$
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t
$$

(4)

Linearization of Equation (4) yields parameters $q_e$ and $k_2$:

$$
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
$$

(5)

### 2.3.3 The Elovich equation


$$
\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)
$$

(6)

where $\alpha$ is the initial adsorption rate (mmoles.g$^{-1}$.hr$^{-1}$) and $\beta$ is the desorption constant (g.mmoles$^{-1}$) during any one experiment. A simplified version of Equation (6) results after applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t = t$ and assuming that $\alpha\beta t >> 1$:

$$
q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t
$$

(7)

Equation (7) should be a linear plot between $q_t$ and $\ln(t)$, with $\beta$ and $\alpha$ obtained from the slope and the intercept, respectively.

### 2.3.4 The intraparticle diffusion model

This model refers to the theory proposed by Weber & Morris (1963) and it is expressed as:

$$
R = k_{id} (t)^a
$$

(8)

The linearized form of the above equation is:

$$
\log R = \log k_{id} + a \log t
$$

(9)

where $R$ is the percent copper ion adsorbed, $a$ is the gradient of linear plots and $k_{id}$ is the intraparticle diffusion rate constant, hr$^{-1}$.

### 2.3.5 Total titratable negative surface charge

3. RESULTS AND DISCUSSION

3.1 Carbon adsorption properties

In this study, swine manure-based carbons, SMC were produced by steam-activation to various degrees of activation by changing both the water flow rate and activation time. From the adsorption capacities estimated by the Langmuir model, Lima, I.M. and Marshall, W.E., 2007 have shown that 20 mM ion concentrations were sufficient to saturate the SMC binding sites. In the current study SMC were further exposed to four metal ions, both individually and in a competitive mode, at 5 mM concentrations (Tables 1, 2). Values reported are means of duplicate determinations where the standard error was ±1% of the mean values. Swine manure-based activated carbons generally showed good metal ion adsorption at pH 4.8 with the exception of nickel. Carbons performed better when exposed to single metal ion solutions than when in a competitive mode. In either case they had more affinity towards copper, followed by zinc, and then cadmium ions (Figure 1). There is no apparent reason why nickel ions bind much less readily than the remaining 3 metal ions in this study, as it is an ion of similar size and weight. Carbons made from poultry manure did not readily adsorb nickel ions as well (Lima, I.M. & Marshall, W.E., 2005c). Nickel being removed less readily than other heavy metals has also been previously noted by Brown, M.J. & Lester, J.N., 1979 and Ho, Y.S., Wase, D.A.J. & al, 1995 but no reasons for that were suggested.

The degree of activation changes with the activation time and flow rate, however, no specific trends between activation conditions and adsorption were obvious (Tables 1 and 2). For a 30 minute activation, adsorption for all metals individually, increased when flow rate was increased from 1 to 3 ml/min, but decreased from 3 to 5 ml/min. At 60 min activation, and interestingly, the opposite effect happened, with adsorption consistently decreasing from 1 to 3 ml/min activation flow rate, but then increasing from 3 to 5 ml/min. This trend was also present in a competitive mode. When looking at the effect of activation time, at a constant flow rate, adsorption decreased with time of activation, for 3 ml/min but not for 1 and 5 ml/min. At these two flow rates there was an increase in adsorption when going from 30 to 60 min activation.

Table 1. Percent metal adsorbed per gram of swine manure-based carbon, SMC from solutions containing four metal ions at 5mM each.

<table>
<thead>
<tr>
<th>Adsorvent</th>
<th>Metal ion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu^{2+}</td>
</tr>
<tr>
<td>SMC: 30 min at 1ml/min</td>
<td>45.9</td>
</tr>
<tr>
<td>SMC: 60 min at 1ml/min</td>
<td>53.0</td>
</tr>
<tr>
<td>SMC: 15 min at 3ml/min</td>
<td>50.4</td>
</tr>
<tr>
<td>SMC: 30 min at 3ml/min</td>
<td>54.3</td>
</tr>
<tr>
<td>SMC: 45 min at 3ml/min</td>
<td>38.4</td>
</tr>
<tr>
<td>SMC: 60 min at 3ml/min</td>
<td>30.6</td>
</tr>
<tr>
<td>SMC: 30 min at 5ml/min</td>
<td>31.4</td>
</tr>
<tr>
<td>SMC: 60 min at 5ml/min</td>
<td>36.5</td>
</tr>
<tr>
<td>Pur RF</td>
<td>19.6</td>
</tr>
<tr>
<td>Coal</td>
<td>0.0</td>
</tr>
<tr>
<td>Coconut</td>
<td>21.6</td>
</tr>
<tr>
<td>Wood</td>
<td>20.2</td>
</tr>
</tbody>
</table>
Table 2. Percent adsorbed per gram of swine manure-based carbon, SMC from single metal ion 5mM solutions.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Metal ion</th>
<th>Cu²⁺</th>
<th>Cd²⁺</th>
<th>Ni²⁺</th>
<th>Zn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMC: 30 min at 1ml/min</td>
<td>80.3</td>
<td>47.4</td>
<td>3.1</td>
<td>61.5</td>
<td></td>
</tr>
<tr>
<td>SMC: 60 min at 1ml/min</td>
<td>91.8</td>
<td>66.0</td>
<td>5.5</td>
<td>76.8</td>
<td></td>
</tr>
<tr>
<td>SMC: 15 min at 3ml/min</td>
<td>85.9</td>
<td>55.2</td>
<td>1.6</td>
<td>66.7</td>
<td></td>
</tr>
<tr>
<td>SMC: 30 min at 3ml/min</td>
<td>88.3</td>
<td>61.1</td>
<td>2.6</td>
<td>74.2</td>
<td></td>
</tr>
<tr>
<td>SMC: 45 min at 3ml/min</td>
<td>79.9</td>
<td>30.1</td>
<td>2.6</td>
<td>73.5</td>
<td></td>
</tr>
<tr>
<td>SMC: 60 min at 3ml/min</td>
<td>78.5</td>
<td>28.5</td>
<td>4.0</td>
<td>56.1</td>
<td></td>
</tr>
<tr>
<td>SMC: 30 min at 5ml/min</td>
<td>66.8</td>
<td>25.4</td>
<td>4.5</td>
<td>39.7</td>
<td></td>
</tr>
<tr>
<td>SMC: 60 min at 5ml/min</td>
<td>90.0</td>
<td>56.5</td>
<td>5.3</td>
<td>77.0</td>
<td></td>
</tr>
<tr>
<td>Pur RF</td>
<td>28.3</td>
<td>6.9</td>
<td>7.4</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>0.2</td>
<td>11.5</td>
<td>7.2</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>Coconut</td>
<td>24.9</td>
<td>0.0</td>
<td>3.5</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>23.0</td>
<td>2.2</td>
<td>1.2</td>
<td>14.8</td>
<td></td>
</tr>
</tbody>
</table>

Swine manure-based activated carbons generally showed better metal ion adsorption properties than the commercial carbon Pur RF (Tables 1.1, 1.2). Moreover SMC, in general, adsorbed significantly more metal ion than the carbons made from traditional sources and under the same pyrolysis and activation conditions (Figure 1.1). These results indicate that it is the source material (i.e., swine manure) and not pyrolysis and activation conditions which largely determines the carbons ability to adsorb metal ions. In this regard, swine manure as other animal manures (e.g. poultry) has inorganic components such as phosphorous and potassium, not eliminated via pyrolysis. These inorganic components are found in much larger concentrations in manure than in plant based materials such as coal, coconut shells or wood.

During pyrolysis and activation, phosphorous particularly, is concentrated from approximately 1.85% in swine manure to 5.20% in the carbon (Lima, I.M. & Marshall, W.E., 2007). Because these constituents are not completely removed by the acid-wash step, it is likely that they are covalently (chemically) bound within the carbon’s lattice structure. The presence of trapped or covalently bound phosphorus in the form of phosphate groups can create centers of negative charge on the carbon at most pH values.

These centers of negative surface charge seem to be responsible for the ionic binding of the positively charged heavy metals and their mixtures and ultimately enhance the metal ion adsorption properties of the resultant carbons. Carbons’ Surface charge values ranged between 0.54 and 0.86 mmol H⁺ eq.g⁻¹ which are much lower values than it would be expected from the above discussion and the carbon’s ability to sequester positively charged metal ions.

It is possible that other constituents present in the swine manure-based carbons have interfered with the method and additional investigations and/or methods should help understand the unexpected low surface charge values. It is also possible that the method requires additional modifications that take into account the heterogeneous nature of the swine manure-based carbons.
3.2 Adsorption kinetics

Copper ion adsorption by the swine manure-based carbons was monitored over time for discrete times up to 24 hr and it is shown in Figure 1.2 for SMC activated for 45 min at 3 ml/min. It is clear from Figure 1.2 that copper ion uptake was rapid in the first few minutes with approximately 70% of total adsorption occurring in the first 30 minutes. After the first 30 minutes of contact time, adsorption slowed down significantly. Experimental adsorption data was fitted using four different kinetic models in order to investigate which one would give the best representation.
Figure 2 shows the kinetic data for carbons activated for 45 min at 3ml/min fitted with four different kinetic models. It is important to be able to predict the rate at which the adsorbate is removed from solution as this parameter will ultimately control the resident time required for the adsorbent. Residence time is an integral part to the design of any adsorption system. The conformity between experimental data and data predicted by each of four kinetic models studied was expressed by the correlation coefficients. A relatively high correlation coefficient indicates that the model closely describes the kinetics of the observed copper adsorption for the carbons. Resulting kinetic parameters and the goodness of fit are reported in Table 3. Because of the inherent bias resulting from linearization, kinetic parameter sets were determined by nonlinear regression equations of each kinetic model. Nonlinear regression uses error functions to calculate the best fit and proved to be more accurate as higher correlation coefficients were obtained between the model and the experimental data (data not shown). This is true because a nonlinear regression approach provides a mathematically rigorous method for determining the kinetic parameters using the original form of the kinetic equation.

The pseudo first-order model displayed the worst fit of the four studied kinetic models, shown from the \( R^2 \)-values ranging from 0.748 to 0.855. From Figure 1.2 it can be seen that there is a significant deviation from the fitted model at the later stages in the adsorption (\( t > 5 \)hr), where the model plateaus at a lower equilibrium adsorption (\( q_e \)) than the observed experimental data (Table 1.3, Figure 1.2). The pseudo first-order model is based on the rate of adsorption being directly proportional to the difference between the concentration at any time and at equilibrium. However, adsorption is a complex multi-stage process. Enhanced initial uptake occurs, as adsorbate concentration and availability of particularly active surface adsorption sites, are highest. Eventually, as those easier to access adsorption sites become saturated, uptake becomes dependent on the main kinetic (or diffusion) controlling process. The final stage occurs when adsorbate concentration and/or availability of adsorption sites are significantly reduced. An extensive literature review by Ho, Y.S. and McKay, G. (1999) revealed that the pseudo first-order model appears to seldom be the best choice to represent adsorption kinetics. Furthermore, it was observed that this model fits experimental data well for an initial period of the first reaction step only.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1 )</td>
<td>( q_e )</td>
</tr>
<tr>
<td>SMC: 30 min, 1ml/min</td>
<td>11.78</td>
<td>0.359</td>
</tr>
<tr>
<td>SMC: 30 min, 3ml/min</td>
<td>20.66</td>
<td>0.374</td>
</tr>
<tr>
<td>SMC: 45 min, 3ml/min</td>
<td>29.09</td>
<td>0.367</td>
</tr>
<tr>
<td>SMC: 30 min, 5ml/min</td>
<td>18.66</td>
<td>0.283</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elovich</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha )</td>
<td>( \beta )</td>
</tr>
<tr>
<td>SMC: 30 min, 1ml/min</td>
<td>43.83</td>
<td>21.06</td>
</tr>
<tr>
<td>SMC: 30 min, 3ml/min</td>
<td>191.0</td>
<td>23.90</td>
</tr>
<tr>
<td>SMC: 45 min, 3ml/min</td>
<td>1017</td>
<td>29.15</td>
</tr>
<tr>
<td>SMC: 30 min, 5ml/min</td>
<td>79.56</td>
<td>29.03</td>
</tr>
</tbody>
</table>
The pseudo second-order model was a better fit than the pseudo first-order model (Table 3). Interestingly, linearization of the pseudo second-order model gave very high correlation coefficients ($R^2 > 0.99$; data not shown), however, once the kinetic parameters were plugged into the original equation, the deviation of the fitted data to the experimental data was significant and the resulting correlation coefficients ranged between 0.268 to 0.718. A better fit for the pseudo second-order equation was obtained ($R^2$ between 0.819 and 0.942) again, by non-linear regression of the integrated equation resulting in better model estimates $k_2$ and $q_e$. A close inspection of the pseudo second-order fit shows that the deviation from the experimental data is largest at the very beginning of the adsorption stage, as opposed to the pseudo first-order equation. The calculated equilibrium adsorption is still underestimated by the pseudo second-order model (Figure 1.2). This model has been the most widely tested model for the sorption of metal ions and organic pollutants from wastewater since it was proposed (Ho, Y.S. & McKay, G., 1999).

Two other kinetic models were fitted to the experimental data, the Elovich kinetic model and the Intraparticle diffusion kinetic model. The Elovich equation has general application to chemisorption kinetics (Taylor, H.A. & Thon, N., 1952) and available literature has repeatedly demonstrated that this equation has unquestionably widespread utility for its precise in reproducing kinetic data. From Table 1.3 it can be seen that the adsorption data was well represented by the Elovich model, which displayed the best fit of all four models studied ($R^2$ ranging from 0.975 to 0.995). The intraparticle diffusion model also represented the experimental data well ($R^2$ ranging from 0.962 to 0.976). The initial adsorption rate, $\alpha$ obtained from the Elovich kinetic model was significantly higher for carbons activated for 45 min at 3ml/min with $\alpha = 1017$ mmoles.g$^{-1}$.hr$^{-1}$ (Table 1.3). Pseudo first- and second-order models also reported higher kinetic rates for this sample when compared to the rest. Equilibrium concentration was similar for all samples with the exception of carbons activated for 30 min at 5 ml/min, where a lower copper ion uptake resulted in lower concentration at equilibrium. Both the Elovich and the intraparticle diffusion models were good predictors of the adsorption kinetics for $t<24$ hr, yet they are not valid when $t$ is large, as when $t \to \infty, q_t \to \infty$. This means that they do not predict a finite saturation point at large times, as the pseudo first-order and second order models do.

During adsorption, several independent processes occurring either simultaneously or consecutively, such as film, bulk and intraparticle diffusion, and chemical and/or physical sorption will ultimately play a role in the adsorption kinetics. The rate-controlling step for metal ion adsorption can be any of the following scenarios: film diffusion/mass transport around each carbon particle, internal diffusion/mass transport within each particle, and adsorption onto the adsorption site, likely via a chemisorption mechanism. Initially, film diffusion might be the rate-controlling step, gradually leading to how fast adsorption occurs at the adsorption site or to internal diffusion. The kinetic parameters in Table 1.3 are a function of the system variable conditions, and could vary with initial metal ion concentration, agitation speed, carbon particle size, metal solution temperature, pH, etc. The agitation speed was kept at 300 rpm, carbons were ground to less than 325 mesh in size, and pH was buffered at 4.8, which should help to reduce the above rate-limiting steps, enhancing mass transfer and diffusion and ultimately favor the kinetics of adsorption.

4. CONCLUSIONS

This study reports a process for producing activated carbons from swine manure involving pyrolysis and steam activation. The resulting carbons displayed enhanced adsorption ability for metal ions, particularly towards copper ions, exceeding that of plant-based carbons produced...
under the same conditions (79.9% adsorption for copper ions by the swine manure-based carbons versus 0.2%, 24.9% and 23.0% for coal, coconut shell and wood-based carbons, respectively). Pyrolysis, followed by steam activation entraps pre-existing phosphorous found in the manure, in the form of phosphate functional group, in the activated carbon matrix, thus improving the carbon's ability to sequester metal ions. With the presence of several metal ions, competition for adsorption took place and copper ion was still adsorbed the most at 38.4% for the swine manure-based carbon activated for 45 min at 3 ml/min. Results from the kinetic experiments revealed that the kinetics of metal adsorption onto swine manure-based activated carbons were best described by the Elovich Kinetic model with R² values ranging from 0.975 to 0.995.

REFERENCES


