Removal of Lead from Aqueous Solution on Activated Carbon and Modified Activated Carbon Prepared from Dried Water Hyacinth Plant

El-Wakil AM, Abou El-Maaty WM* and Awad FS
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Abstract

In this work, the potential of activated carbon stems and leaves (ACS, ACL) prepared from dried water hyacinth stems and leaves (DS, DL) by chemical activation with phosphoric acid (1:3) and modified activated carbon stems and leaves (MACS, MACL) with nitric acid (1:1) for the removal of lead from aqueous solution was investigated. Carbon samples were produced with a reasonable yield about 75% and have a remarkable surface area (57.46, 71.83, 864.52, 493.78, 381.22, and 265.22 m²/g for DS, DL, ACS, and ACL, MACS and MACL, respectively and well developed pore structure. Batch adsorption experiments were conducted to study the effect of various operating parameters, pH of the solution (1 to 6), initial concentration of lead ions (50 to 400 mg/l), contact time (2-250 min), and temperature (298-323 K). It is obvious that the maximum adsorption of lead at pH 5 is in the order: MACS (175.63 mg/g) > MACL (164.56 mg/g) > DS (90.50 mg/g) > DL (66.60 mg/g) > ACS (36.00 mg/g) > ACL (33.40 mg/g). This may be attributed to the increase in the number of active sites on the modified activated carbon. The equilibrium data were analyzed using Langmuir and Freundlich isotherms. The results showed that the experimental data were fitted well by the Langmuir model. Kinetic results revealed that the adsorption process obeyed a pseudo-second order model and intra-particle diffusion was the rate controlling step. The thermodynamic studies revealed that the adsorption was spontaneous and endothermic process. Desorption of about 90% of the sorbed lead from carbon was achieved using about 0.6 M HCl.

Keywords: Water hyacinth; Activated carbon; Modified activated carbon; Lead; Adsorption

Introduction

The removal of heavy metal contaminants from aqueous solutions is one of the most important environmental concerns because metals are bio refractory, and are toxic to many life forms. Various sources of heavy metals in water are battery manufacturing, basic steel, paper, pulp, metal plating, leather tanning, agrochemicals, petrochemicals, and chemical manufacturing, mining and fertilizer industries. Among the heavy metals, lead is one of the most toxic elements, even at low concentrations. It affects the central nervous system, kidney, liver, and gastrointestinal system, and it may directly or indirectly cause diseases such as anemia, encephalopathy, hepatitis, and the nephritic syndrome [1]. Because of the above factors, there is a necessity to remove these metals from wastewater in order to prevent contamination of natural water bodies by effluents containing toxic metals. The common methods for removing metal ions from water and wastewater include chemical precipitation, oxidation, reduction, reverse osmosis, membrane filtration and adsorption. Among the above methods, the promising process for the removal of metal ions from water and wastewater is adsorption, because the employed adsorbent can be regenerated by suitable desorption process and it is highly effective and economical [2].

Activated carbon is one of the most popular adsorbents for the removal of metal ions from aqueous solutions. Currently, activated carbon is widely used as an adsorbent in wastewater treatments. It has highly developed porosity, a large internal surface area, and relatively high mechanical strength. Despite its widespread use in industries, activated carbon remains an expensive material. Therefore, it is necessary to investigate and develop low-cost effective carbons that can be applied to water pollution control. The properties such as surface charge, type of surface functional groups, specific surface area, and pore-size distribution affect the adsorption capabilities of metal ions on activated carbon. All above mentioned physical and chemical properties of activated carbon depend on the precursor materials and activation methods used [3].

In this article, the possibility of using dried water hyacinth, Carbonized (stems, leaves) and modified Activated Carbon (stems and leaves) as efficient adsorbents for removal of Pb²⁺ from aqueous solution will be investigated. The effects of pH, initial Pb²⁺ concentration, and temperature and contact time on adsorption capacities were also examined. The study was conducted using first order kinetics, pseudo-second order kinetics and intra-particle diffusion model. Also, equilibrium isotherm data were analyzed according to Langmuir and Freundlich equations.

Experimental

Materials and reagents

Stock solution of Lead containing 1 mg lead cm⁻³ was prepared by dissolving 1.5984 g of Pb(NO₃)₂ (supplied by BDH) in distilled water and this solution was complete up to the mark of 1 L measuring flask. Lead solutions of lower concentrations were prepared by further dilution with distilled water. PAR(2-pyridyl azo resorcinol) solution

*Corresponding author: Dr. Weam Mahmoud Abou El-Maaty, Lecturer of Analytical Chemistry, Faculty of Science, P.O.Box: 35516, Mansoura University, Egypt. Tel: (+2) 0100262722-0109986635; Fax: (050) 2224132-2246254; E-mail: dr.wream_elmaaty@yahoo.com

Received February 21, 2014; Accepted March 28, 2014; Published March 31, 2014


Copyright: © 2014 El-Wakil AM, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
0.1% (w/v) prepared by dissolving 0.1 g of solid substance in least amount of distilled water then transfers to 100 ml measuring flask and complete to the mark using distilled water. All other chemicals used were of analytical grades.

**Preparation of adsorbents**

**Preparation of dried water hyacinth (DS and DL):** The plant water hyacinth was collected from Canal extended from river Nile in Mansoura, Egypt. The roots of the plant were removed while the leaves and stems were washed with water then with distilled water and were soaked in 0.25 M EDTA at pH 10 overnight for removing any metal ions adsorbed on the plant (stems and leaves) and washed with distilled water for several times and dried in oven at 110°C for 48 h then dried stems (DS) and leaves (DL) were ground and stored in desiccators till used in adsorption experiments.

**Preparation of chemically activated carbon stems (ACS) and leaves (ACL):** The dried phase was impregnated into 3 times its wt. with concentrated H3PO4 at room temperature for 2 days. Then dried in oven at 110°C for 48 h then placed in a muffle oven (in a stainless steel reactor) where the samples were heated gradually in absence of air at a rate of heating=10 K/min up to 550-600°C and then maintained at this temperature for 3 h. After cooling to room temperature, the activated carbon obtained was washed thoroughly with distilled water until the pH of the supernatant become steady at about (pH=6). The samples were dried at 110°C for 24 h. Finally, the activated carbon prepared from stem (ACS) and leaves (ACL) were ground and stored in desiccators till used in adsorption experiments.

**Modification of the activated carbon stems (MACS) and leaves (MACL):** The activated carbon (ACS and ACL) were modified by surface oxidation with concentrated nitric acid (1:1 dilution from 67% concentrated HNO3). The modification procedure was as follows. A known volume of 1:1 diluted nitric acid was heated at 110°C. The appropriate amount of ACS or ACL was added to the boiling nitric acid solution at a ratio of 1 g AC to 5 ml nitric acid solution. It was treated for 3 h to increase the formation of functional groups, such as carboxylic acids. The residual material was washed with distilled water until the pH of the supernatant become steady at about (pH=6). The modified activated carbon by using nitric acid was then dried at 120°C for 24 h and then were ground and stored in desiccators till used in adsorption experiments.

**Batch adsorption experiments**

Adsorption isotherms were studied by adding 0.025 g of DS, DL, ACS, ACL, MACS and MACL into 25 ml solutions with initial concentrations of Pb (II) ranging from 5 to 400 mg/L. The initial pH values of the solutions were adjusted from 1.5 to 6 using 0.01 M HNO3 and 0.01 M NaOH.

To study the effects of pH on Pb (II) adsorption, 0.025 g of the adsorbent were dispersed into 25 ml solutions containing 250 mg/L of Pb(II). The initial pH values of the solutions were adjusted from 1.5 to 6 using 0.01 M HNO3, and 0.01 M NaOH.

Kinetic experiments were performed by using different flasks containing around 0.2 g of adsorbent in 200 ml solutions containing 200 mg/L of Pb2+. At desired time intervals, 1 ml of aliquots were taken from the suspension and the concentration of Pb2+ is determined spectrophotometrically as described above.

**Result and Discussion**

**Characterization of prepared samples**

Physico-chemical characterization of MACS, MACL, ACS, ACL, DS and DL were determined as follow: moisture content determined using oven drying method, point of zero charge (pHpzc), surface area was determined from the application of Brunauer Emmett and Teller (BET) equation to the adsorption-desorption isotherm of N2 at 77k [5], as shown in (Table 1). The morphology of MACS, MACL, ACS, ACL, DS and DL were examined by electron microscopy is shown in Figure 2. Examination of SEM micrographs obtained clearly indicate the porous structure of different adsorbents at magnification of 1500x, 3500x and 10000x for (DS and DL), (ACS and ACL) and (MACS and MACL), respectively. The FT-IR spectra for similar samples are shown in Figure 1. All samples show wide band at about (3373-3442 cm−1) due to O-H stretching mode of hexagonal group and adsorbed water. The shoulders observed at (2849-2932 cm−1) due to aliphatic (C-H) and appear for all samples [6]. The bands near 1600 cm−1 is due to C=C stretching vibration in aromatic ring and is observed for all samples. The bands at (1711-1713 cm−1) for MACL and MACS are due to stretching vibration of carboxyl groups on the edges of layer plane [7]. The weak bands appearing at 1580, 1574, 1240, 1520, 1608, 1243, 1530 and 1621 cm−1 are due to formation of highly conjugated (C=O stretching, C-O stretching in carboxylic groups and carboxylate moieties) [8].

**Adsorption parameters**

**Effect of pH:** To optimize the pH for maximum removal efficiency and to avoid the precipitation of Pb (II), a sorption experiment was conducted in the initial pH range from 2 to 6, as shown in Figure 3. The amount adsorbed by DS increased from 21.04 to 102.50 mg/g, for sample DL from 17.10 to 68.04 mg/L at pH=2 and 5, respectively. At low pH, the surface of the adsorbent was surrounded by hydronium ions that compete with metal ions, which prevented the metal ions from approaching the binding sites on the adsorbent.

Where \( q_e \) is the amount of Pb2+ adsorbed (mg/g), \( C_o \) and \( C_e \) are the initial and equilibrium liquid-phase concentrations of Pb2+ (mg/g), respectively. \( V \) is the volume of the solution (L), and \( m \) is the weight of the sorbent used (g).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Moisture content %</th>
<th>Surface pH</th>
<th>Surface Area m2/g</th>
<th>Total pore volume</th>
<th>pH PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS</td>
<td>6.71</td>
<td>5.95</td>
<td>57.46</td>
<td>0.01</td>
<td>4.95</td>
</tr>
<tr>
<td>DL</td>
<td>5.1</td>
<td>6.13</td>
<td>71.83</td>
<td>0.03</td>
<td>4.80</td>
</tr>
<tr>
<td>ACS</td>
<td>3.88</td>
<td>4.50</td>
<td>864.52</td>
<td>0.52</td>
<td>4.05</td>
</tr>
<tr>
<td>ACL</td>
<td>2.64</td>
<td>4.10</td>
<td>493.78</td>
<td>0.31</td>
<td>4.05</td>
</tr>
<tr>
<td>MACS</td>
<td>9.13</td>
<td>3.60</td>
<td>381.22</td>
<td>0.43</td>
<td>3.38</td>
</tr>
<tr>
<td>MACL</td>
<td>7.89</td>
<td>4.00</td>
<td>365.22</td>
<td>0.29</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Table 1: Characteristics of the dried Water hyacinth (stems and leaves), activated carbon and modified activated carbon (stems and leaves).
The increase in metal removal as pH increases can be explained on the basis of a decrease in competition between hydronium ions and metal species for the surface sites. At pH=5.0, the adsorption capacity of (DS, DL, ACS and ACL) almost reaches the maximum value. Because the speciation diagram of lead shows that at pH>6.0 the species such as [Pb(OH)]\(^+\), [Pb\(_3\)(OH)\(_4\)]\(^+\), and [Pb(OH)\(_2\)]\(^-\) will be produced [9]. In order to guarantee to truly examine the adsorption property of carbon samples as well as to avoid precipitation of Pb(II) ions, all the following experiments were conducted at pH=5.0.
Figure 4: Effect of initial metal concentration on the removal of Pb$^{2+}$ by (a) DL, (b) DS, (c) ACL, (d) ACS, (e) MACL and (f) MACS. (Conditions: $C_0=50$-400 mg/l, $T=25^\circ$C; adsorbent dose=0.025 g/25 ml).
Figure 5: Effect of temperature on adsorption capacity of Pb\(^{2+}\) by DS, DL, ACS, ACL, MACS and MACL (Conditions: \(C_0=50-400\) ppm; adsorbent dose=0.025 g/25 ml).
Effect of initial concentration on the uptake of Pb^{2+}

The effect of initial concentration on adsorption was investigated, as illustrated in Figure 4 and 5. It is revealed that, as the initial concentration increased, the adsorption capacities increased. The initial concentration may provide the driving force to overcome the resistance of the mass transfer of Pb(II) between liquid and solid phases [10]. The initial concentration was higher, and then the driving force was higher, and therefore the adsorption capacity would be higher.

Effect of temperature on adsorption

The effect of solution temperature on Pb^{2+} removal was studied at three different temperatures: 298 K, 313 K and 323 K using DS, DL, ACS, ACL, MACS and MACL. The results are presented in Table 2, and it is obvious from the table that increasing the temperature significantly affected the amount of Pb^{2+} adsorbed from solution by different adsorbents. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbate and adsorbent sites or the increased rate of intra particle diffusion of Pb^{2+} molecules into the pores of the adsorbents as a result of decreasing solution viscosity at higher temperatures and the number of adsorption sites generated because of some internal bonds near the edge of surface active sites of sorbent [11,12].

Effect of contact time on adsorption

Figure 6 shows the effect of contact time on the percent removal of Pb^{2+} by (a) DS and DL, (b) ACS and ACL, (C) MACS and MACL at 25°C using a sorbent concentration of 1 g/L at pH 5. The initial concentration of Pb^{2+} was 200 ppm. It is obvious that, the adsorption amount of Pb(II) rapidly increased at the beginning of adsorption; more than 65% of the adsorption capacities of corresponding adsorbents for Pb^{2+} occurred within 5 min for DS and DL, and more than 88% occurred within 5 min for ACS and ACL, and about 90% occurred within 15 min for MACS and MACL. Pb^{2+} uptake almost remained constant after 60 min for MACS, MACL, ACS and ACL, and after 90 min for DS and DL so 90 min could be considered the equilibrium time of the Pb(II) adsorption. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of metal ions to the surface of adsorbent particles and the availability of the uncovered surface area and the active sites on the adsorbent.

Effect of initial concentration on the uptake of Pb^{2+}

Effect of temperature on adsorption

Effect of contact time on adsorption

<table>
<thead>
<tr>
<th>Samples</th>
<th>Qe (mg g^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
</tr>
<tr>
<td>DS</td>
<td>90.50</td>
</tr>
<tr>
<td>DL</td>
<td>66.60</td>
</tr>
<tr>
<td>ACS</td>
<td>36.00</td>
</tr>
<tr>
<td>ACL</td>
<td>33.40</td>
</tr>
<tr>
<td>MACS</td>
<td>175.63</td>
</tr>
<tr>
<td>MACL</td>
<td>164.56</td>
</tr>
</tbody>
</table>

Table 2: Effect of temperature on maximum adsorption capacities of Pb^{2+} be DS, DL, ACS, ACL, MACS and MACL.
Effect of adsorbent dosage

The effect of amount of DS, DL, ACS and ACL on the removal percentage of Pb$^{2+}$ was shown in Figure 7. It could be clearly seen that, an increase in sorbent dose is in favor of Pb$^{2+}$ removal. When the sorbent dose increases from 0.05 to 0.25 g, the percent Pb$^{2+}$ removal by DS, DL, ACS and ACL increase from 48.40% to 96.36 %, from 31.01% to 95.63%, from 17.9 % to 53.95% and from 16.46% to 50.95%, respectively. Increase in adsorption with adsorbent dosage can be attributed to increased adsorbent surface area and availability of more adsorption sites.

Adsorption isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. Adsorption isotherm is important to describe how adsorbates interact with adsorbents and so it is important in optimizing the use of adsorbents. Two common isotherm equations namely, Langmuir and Freundlich models were tested [13-15].

The Langmuir isotherm assumes a surface with homogeneous binding sites equivalent sorption energies, and no interaction between adsorbed species. Its mathematical form is written as:

$$\frac{C_e}{q_e} = \frac{1}{Q} + \frac{C_e}{Q_{max}}$$

Where $q_e$ is the amount adsorbed at equilibrium (mg g$^{-1}$), $C_e$ is the equilibrium concentration of the lead (mg L$^{-1}$), constant $b$ is related to the energy of adsorption (Lmg$^{-1}$), $Q$ is the Langmuir monolayer adsorption capacity (mg g$^{-1}$). The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor $RL$.

$$RL = \frac{1}{1 + bC_o}$$

$C_o$ is the highest initial solute concentration, $b$ is Langmuir adsorption constant (L/mg). $RL$ indicates the type of isotherm to be reversible (RL=0), Favorable (0<RL<1), Linear (RL=1) or unfavorable (RL>1) [16].

The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. It is represented as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

Where $q_e$ is the amount adsorbed at equilibrium (mg g$^{-1}$), $C_e$ is the equilibrium concentration of lead (mg L$^{-1}$), $K_f$ is roughly an indicator of the adsorption capacity, and $1/n$ is the adsorption intensity. A linear plot of $\ln q_e$ versus $\ln C_e$ confirms the validity of the Freundlich model.

![Figure 7: Effect of sorbent dosage on the removal of Pb$^{2+}$ by DS, DL, ACS and ACL. (Conditions: T=25°C; $C_0$=200 mg/l, $V$=50 ml; time=7 h).](image)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Langmuir parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>MACS</td>
<td>0.999</td>
</tr>
<tr>
<td>MACL</td>
<td>0.999</td>
</tr>
<tr>
<td>ACS</td>
<td>0.988</td>
</tr>
<tr>
<td>ACL</td>
<td>0.984</td>
</tr>
<tr>
<td>DS</td>
<td>0.999</td>
</tr>
<tr>
<td>DL</td>
<td>0.999</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>MACS</td>
<td>0.773</td>
</tr>
<tr>
<td>MACL</td>
<td>0.894</td>
</tr>
<tr>
<td>ACS</td>
<td>0.992</td>
</tr>
<tr>
<td>ACL</td>
<td>0.987</td>
</tr>
<tr>
<td>DS</td>
<td>0.926</td>
</tr>
<tr>
<td>DL</td>
<td>0.948</td>
</tr>
</tbody>
</table>

The Freundlich isotherm is more suitable to explain the adsorption of Pb$^{2+}$ onto different adsorbents calculated from the Langmuir model are all the same as the experimental data. Also, RL values obtained are in the range of (0.000-0.086), thereby confirming that the adsorption is a favorable process. It can be concluded that the monolayer Langmuir adsorption isotherm is more suitable to explain the adsorption of Pb$^{2+}$ onto different adsorbents.

Adsorption kinetics

The pseudo-first order equation and the pseudo-second order equation: In order to investigate the controlling mechanism of adsorption process of Pb$^{2+}$ by DS, DL, ACS, ACL, MACS and MAACL, the pseudo-first order and the pseudo-second order kinetic models were cited to evaluate the experimental data. The pseudo-first order kinetic model has been widely used to predict metal adsorption kinetics. It was suggested by Lagergren [17] for the adsorption of solid/liquid systems. The differential form of the pseudo-first order model of adsorption can be expressed as:

$$\frac{dq}{dt} = k_1 (q_e - q)$$

where $q$ is the amount of adsorbate adsorbed at time t (mg g$^{-1}$), $q_e$ is the monolayer capacity (mg g$^{-1}$), $t$ is the time (min), and $k_1$ is the pseudo-first order rate constant (g mg$^{-1}$ min$^{-1}$).
Figure 8: Langmuir plot for the adsorption of Pb²⁺ by (a) DS, DL (b) ACS, ACL (C) MACS, MACL.

Figure 9: Freundlich plot for adsorption of Pb²⁺ by a) DS,DL (b) ACS, ACL (C) MACS, MACL.
Where \( q_e \) and \( q_t \) (mg/gm) are the amounts of lead adsorbed at equilibrium and at time \( t \), respectively and \( k_1 \) is the equilibrium constant (min\(^{-1}\)). Integration of equation (6) and by applying the initial conditions \( q_t = 0 \) at \( t = 0 \) and the linear form can be formulated as [18]:

\[
\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}
\]  

Where \( q_e \) is the adsorption uptake of Pb\(^{2+}\) at time \( t \) (mg/g) and \( k_1 \) (min\(^{-1}\)) is the rate constant of the pseudo-first-order adsorption. A plot of \( \log (q_e - q_t) \) versus \( t \) should be linear; the parameters \( k_1 \) and \( R^2 \) (correlation coefficient) calculated from the data (Figure 10) are listed in Table 5. It can be seen that the linear correlation coefficients (\( R^2 \)) for the pseudo-first order kinetic model are high. However, there are large differences between the experimental \( q_e \) values (\( q_e,\text{exp} \)) and the calculated \( q_e \) values (\( q_e,\text{cal} \)), which indicated the pseudo-first order kinetic model was poor fit for the adsorption processes of DS, DL, ACS, ACL, MACS and MACL for Pb\(^{2+}\). The differential form of the pseudo-Second order reaction equation may be written as [18,19]:

\[
\frac{dq_e}{dt} = k_2 (q_e - q_t)^2
\]

After integration considering the boundary conditions the linearized form of this model can be expressed as [18]

\[
\frac{t}{q_t} = K q_e + \frac{t}{q_e}
\]

Where \( k_2 \) (g mol\(^{-1}\) min\(^{-1}\)) is the rate constant of pseudo-second-order adsorption. Figure 11 shows the plot of \( t/q \) versus \( t \) for Pb\(^{2+}\) onto DS, DL, ACS, ACL, MACS and MACL. It can be observed from Table 6 that \( R^2 \) values for the pseudo-second order kinetic model are all over 0.999, moreover, the \( q_e,\text{cal} \) values for the pseudo-second order kinetic model are all consistent with the \( q_e,\text{exp} \) values. These suggested that the adsorption processes of DS, DL, ACS, ACL, MACS and MACL for Pb\(^{2+}\) can be well described by the pseudo-second order kinetic model. These suggested that the pseudo-second-order adsorption mechanism was predominant referring that adsorption process is controlled by chemisorption which involves valence forces through sharing or...
Figure 11: Pseudo-second-order model for the adsorption of Pb$^{2+}$ by (a) DS, DL (b) ACS, ACL and (c) MACS, MACL.

Figure 12: Bt versus t plot for adsorption of Pb$^{2+}$ on DS, DL, ACS, ACL, DL, MACS, MACL at 200 ppm.
exchange of electron between the solvent and the adsorbate. Since neither the pseudo-first-order nor the second-order model can identify the diffusion mechanism, the kinetic results were further analyzed by the intra-particle diffusion mode to elucidate the diffusion mechanism.

**Intra-particle diffusion model:** Adsorption is a multi-step process involving transport of solute molecules from the aqueous phase to the surface of the solid particles of adsorbent, and then diffusion of the solute molecules into the interior of the pores, which is likely to be a slow process, and is therefore, rate determining. The intra-particle diffusion parameter, \( K_d \) (mg g\(^{-1}\) h\(^{-0.5}\)) is defined by the following equation [20]:

\[
q_t = K_d t^{0.5} + C
\]

(10)

Where \( K_d \) is the intra-particle diffusion rate constant (mg g\(^{-1}\) h\(^{-0.5}\)) and C is a constant. According to this model, \( qt \) versus \( t^{0.5} \) should be linear if intra-particle diffusion is involved in the adsorption process. From Eq. (10), if pore diffusion is the rate limiting step, then a plot of \( qt \) against \( t^{0.5} \) must give a straight line with a slope that equals \( k_d \) and the intercept value C represents the resistance to mass transfer in the external liquid film.

Figure 12 shows the plot of \( qt \) against \( t^{0.5} \) for adsorption of 200 ppm Pb\(^{2+}\) by DS, DL, ACS, ACL, MACS and MACL, the plots are multi-linear, containing at least three linear segments which indicate that three steps occur during adsorption process. The first sharper portion is transport of Pb\(^{2+}\) from the bulk solution to the adsorbent external surface by diffusion through the boundary layer (film diffusion). The second portion is the diffusion of Pb\(^{2+}\) from the external surface into the pores of the adsorbent. The third portion is the final equilibrium stage, where Pb\(^{2+}\) were adsorbed on the active sites on the internal surface of the pores and the intra-particle diffusion starts to slow down due to the solute concentration getting lower and lower in solution. In addition, the linear portions of curves did not pass through the origin suggesting that pore diffusion is not the step controlling the overall rate of mass transfer at beginning of adsorption.

In Table 7, the correlation coefficients \( (R^2) \) for the linear segment intra-particle diffusion model were between 0.563 and 0.975, indicating that the intra-particle diffusion was not the only rate-controlling step; other process could control the rate of adsorption. The boundary layer effect may control the rate of mass transfer in the time period of the first linear segment; this conclusion could be corroborated by the analysis of data from Boyd’s model.

The model of Boyd is expressed as [21]:

\[
F = 1 - \frac{6}{\pi^2} \exp \left( 1 - Bt \right)
\]

(11)

<table>
<thead>
<tr>
<th>Intraparticle diffusion model</th>
<th>Boyd model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorbent code</strong></td>
<td>( R^2 )</td>
</tr>
<tr>
<td>MACS</td>
<td>0.563</td>
</tr>
<tr>
<td>MACL</td>
<td>0.590</td>
</tr>
<tr>
<td>ACS</td>
<td>0.872</td>
</tr>
<tr>
<td>ACL</td>
<td>0.520</td>
</tr>
<tr>
<td>DS</td>
<td>0.954</td>
</tr>
<tr>
<td>DL</td>
<td>0.975</td>
</tr>
</tbody>
</table>

Table 7: Intraparticle diffusion parameters for adsorption of Pb(II) by DS, DL, MACS and MACL at 200 ppm.
Where $F$ is the fractional attainment of equilibrium, at different times, $t$, and $Bt$ is a function of $F$.

$$F = \frac{q_t}{q_e}$$

Where $q_t$ and $q_e$ are the metal uptake (mmol g$^{-1}$) at time $t$ and at equilibrium, respectively.

Equation (18) can be rearranged to [22]

$$B_t = -0.4977 - \ln (1 - F)$$

Figure 13 shows the values of $B_t$ were calculated from Eq. (13) and plotted against time $t$. The linearity of this plot can provide available information to distinguish intra-particle diffusion and boundary layer effect (film diffusion) rates of adsorption. If a plot of $B_t$ versus $t$ is a straight line passing through the origin, then adsorption will fit layer effect. The plots are linear only in the initial period of adsorption and do not pass through the origin, indicating that external mass transfer is the rate limiting process in the beginning of adsorption and then is the intra-particle diffusion.

**Thermodynamic study**

The data obtained from the temperature study were used for thermodynamic analysis. Thermodynamic parameters such as change in standard free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy($\Delta S^\circ$) were determined using the following eqs [23]:

The van’t Hoff equation

$$\ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$K_d = \frac{q_e}{c_e}$$

Where $K_d$ is the adsorption coefficient, $\rho=1000$ g/L to make dimensionless $K_d$ [24]. $\Delta G^\circ$ (J/mol) is the change in Gibbs Free Energy, $\Delta H^\circ$(J/mol) is the enthalpy change of Pb$^{2+}$ adsorption, $\Delta S^\circ$ (J/molK) is the entropy change of Pb$^{2+}$ adsorption, $R$ is the universal gas constant (8.314 J/mol K) and $T$ is the absolute temperature (K).

By plotting a graph of $\ln K_d$ versus $1/T$ (Figure 14), the values of $\Delta H^\circ$ and $\Delta S^\circ$ can be estimated from the slope and intercept of van’t Hoff plots, respectively. The thermodynamic parameters are given in Table 8. It is clear from the table that the values of $\Delta G^\circ$ are negative for DS, DL, ACS, ACL, MACS and MACL. The negative values of $\Delta G^\circ$ at various temperatures indicate the spontaneous nature of the sorption process. The fact that the values of the $\Delta G^\circ$ decrease with increasing temperature indicates the increase of spontaneous effect. For all the sorbents, the positive value of $\Delta H^\circ$ suggested the endothermic nature of the adsorption process. Moreover, the positive values of $\Delta S^\circ$ point out the increased randomness at the solid/liquid interface during the sorption of Pb$^{2+}$ by DS, DL, ACS, ACL, MACS and MACL.

**Desorption studies**

To achieve practical and economical adsorption, a promising adsorbent is required to have not only high adsorption capacity but also regeneration ability for recycling use. The use of thermal activation to regenerate the adsorbent could require high energy and result in a 5-10% adsorbent loss in each cycle. Hence, Studies were attempted to use chemical regeneration for adsorbate desorption [25]. Desorption of Pb using HCl as a desorbing agent by disruption coordination of metal ions and subsequent release from the activated carbon surface into the desorption medium was studied. In order to investigate the desorption capacity of different adsorbents, 0.025 g of different adsorbents were introduced to 25 ml solution of 200 ppm of lead at pH 5. As the adsorption reaches equilibrium, the metal ion concentration of the solution was measured, Then, the adsorbent loaded with lead was collected and treated with 25 ml×M HCl to remove the adsorbed Pb$^{2+}$. The results relating to desorption of lead by HCl of different concentrations are shown in Tables 9 and 10. The results show that increase in concentration of HCl. The desorption also increased but remained constant with 0.6 M HCl.

**Comparison of the adsorption capacities of sorbents toward Pb$^{2+}$**

Table 11 lists the comparisons of maximum adsorption capacities of Pb$^{2+}$ on DS, DL, ACS, ACL, MACS and MACL obtained in this study with various adsorbents previously used for the adsorption of Pb$^{2+}$ [26,27]. The MACS and MACL have a higher adsorption capacity than that of the most other adsorbents reported in the literature, suggesting that it may be potential for Pb$^{2+}$ removal from aqueous solution.
Based on the results, it is clear that the adsorption of lead ions onto various adsorbents was found to be pH-dependent. The adsorption process was an endothermic process. Desorption of Pb^{2+} using 0.6 M HCl as a desorbing agent by disruption coordination of metal ions and subsequent release from the activated carbon surface into desorption medium was studied.

**References**


17. Lagergren S (1898) Zur theorie der sogenannten adsorption gelöster stoffe.


