Full Length Research Paper

Utilization of maize (Zea mays) cob as an adsorbent for lead (II) removal from aqueous solutions and industrial effluents

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Maize cob was used as an adsorbent in order to evaluate its potential for the removal of lead from aqueous solutions and effluents from battery and paint industries with Dowex (synthetic resin) as control. Experimental data were analyzed in terms of Freundlich isotherm model. Equilibrium was attained at 2 h and adsorption rate constants for maize cob and dowex were 7.26 x 10⁻² and 7.58 x 10⁻² min⁻¹, respectively. Equilibrium pH value was 6; shaking at 150 rpm enhanced adsorption with maximum adsorption by both adsorbents in battery and paint effluents. Optimal weight at equilibrium for the adsorbents in Pb²⁺ solution was 16 mg/L of solution. Pb²⁺ removal by maize cob from battery effluent was 99.99% while it was 47.38% for Dowex. Corresponding values from paint effluents were 66.16 and 27.83%. The study concludes that maize cob has great potentials to remove Pb²⁺ from industrial effluents.

Key words: Adsorption, lead, maize cob, wastewaters.

INTRODUCTION

Lead (Pb) and its compounds are widely used in the industries, hence they are commonly found in air, water, soil and food (Yu et al., 2001). Pb may get into the aquatic environment through sources like smelters, industrial effluents from battery, paint, plastic, textiles, microelectronics, etc (Prasad and Freitas, 2000). Pb is a heavy metal of great environmental concern and poses threat to plants, animal and human health due to its bioaccumulative tendency and toxicity (Horsfall and Spiff, 2004). Pb has no known beneficial biochemical attribute (Harrison et al., 1993) and it is known to have toxic effect on the nervous system, kidney and liver (Shukla and Pai, 2005).

Pb, being a heavy metal, tends to accumulate in the food chain because of its persistent nature, and it is therefore necessary to remove it from waste water (Cossich et al., 2002). Although various treatment techniques have been employed to treat wastewater, most of the methods suffer some drawbacks such as expensive generation of secondary pollutants and ineffectiveness for low metal concentration (Han et al., 2006). Different materials have been used for heavy metal pollution abatement in different parts of the world. They include anaerobically digested sludge (Tokcaer et al., 2006), bacteria (Lu et al., 2006), fungi (Garcia and Alonso, 2005), algae (Sune et al., 2007), amongst others. Agricultural waste materials have also attracted attention of researchers as biosorbents for the removal of heavy metals in wastewaters (Horsfall et al., 2003; Horsfall et al., 2004; Kar and Misra, 2004; Khan and Wahab, 2007; Khormaei et al., 2007; Nouri et al., 2007; Uysal and Ar, 2007). Waste products from seafoods have also been used (Lu et al., 2007).

Maize (Zea mays) cob was selected for this study because of its relative abundance in Nigeria. Maize is a major staple cereal in Nigeria and therefore, produces large volume of waste. Maize is widely believed to have
the greatest potential among food crops for attaining the technological breakthroughs that will improve food production (Smith et al., 1997). Almost all the different uses of maize dispose off the cobs. The cobs were therefore used as potential adsorbents for Pb sup2+ removal from wastewater particularly since conventional methods are expensive. Therefore, the need to develop cheaper methods in a developing country like Nigeria becomes imperative.

EXPERIMENTAL

Reagents, materials, effluents and instrumentation

All chemicals used were of analytical grade. A 1000 mg/L stock solution of Pb sup2+ was prepared from Pb(NO
sub3)2 supplied by Nice Chemicals Ltd., Cochin, India. Standard Pb sup2+ solutions in the range 20 – 600 mg/L were then prepared from stock solution. Dowex, the synthetic resin used was supplied by BDH-Dow Chemical Co., Midland, USA. Batch samples of maize cobs were collected as waste materials from households. The cobs were thoroughly washed first with tap water and then, with distilled – deionized water; dried to constant weight and ground to pass through a 22- mesh sieve (Dakiky et al., 2002). Batch samples of battery and paint effluents (with initial Pb sup2+ concentrations of 8.96 and 9.45 mg/L respectively) were collected from points of discharge of effluents into the environment at Ikeja Industrial Estate, Lagos – Nigeria. A Jenway model 3015 pH meter (Jenway Ltd., Dunmpw Essex, England) was used to measure the pH of solutions. Pb sup2+ concentration was measured by Alpha 4 Atomic Absorption Spectrophotometer (Chemtech Analytical, UK) using hollow cathode lamp.

Adsorption experiments

Equilibrium conditions of adsorbents weight (capacity studies), contact time (kinetics), pH and adsorbate (Pb sup2+) concentrations (equilibrium isotherm) were studied using Pb sup2+ standard solutions and industrial (battery and paint) effluents.

Kinetic studies

Kinetic parameters for the adsorption process were studied on batch adsorption of 100 mg/L Pb sup2+ at 32°C. A 0.4 g aliquot of the maize cob was added to 25 ml of 100 mg/L Pb sup2+ at pH 5 in a 100 ml conical flask. Contact time was varied between 30 min to 3 h at 30 min intervals. The mixture was then filtered thereby separating adsorbent and the filtrate analyzed for residual Pb sup2+; thereafter, the percent removal of Pb sup2+ was estimated (Addour et al., 1999; Brown et al., 2000; Kok et al., 2001; Dakiky et al., 2002; Horsfall et al., 2003; Kadirvelu and Namasivayam, 2003). The pH values investigated were 2, 3, 4, 5, 6 and 8. A 0.4 g aliquot of maize cob was weighed and added to 25 ml of 100 mg/L Pb sup2+ solution at the desired pH and left for 2 h. The mixture was then filtered and the filtrate analyzed for Pb sup2+. The procedure was repeated for each of the crop residues and carried out in duplicates (Akhtar et al., 2004; Horsfall and Spiff, 2004; Iihan et al., 2004; Cho et al., 2005).

Effect of pH on adsorption capacity

A 100 mg/L Pb sup2+ solution was prepared from 1000 mg/L stock solution; the pH of the solution was adjusted to desired value and kept constant with the addition of either 0.1 M NaOH or 0.1 M HCl. The pH values investigated were 2, 3, 4, 5, 6 and 8. A 0.4 g aliquot of maize cob was weighed and added to 25 ml of 100 mg/L Pb sup2+ solution at the desired pH and left for 2 h. The mixture was then filtered and the filtrate analyzed for Pb sup2+. The procedure was repeated for each of the crop residues in duplicates.

Effect of concentration on adsorption

Pb sup2+ standard solutions with concentration range of 20 – 600 mg/L were prepared from the stock solution. Adsorbent weight of 0.4 g in 25 ml solution was also used for adsorption isotherm studies with a contact period of 2 h (earlier established as equilibrium time or adsorption) after which the mixture was filtered for analysis for Pb sup2+ (Brown et al., 2000; Goksungur et al., 2003; Horsfall and Spiff, 2004). The experiment was repeated for each of the crop residue in duplicates.

Effect of shaking period

The experiment was carried out to study the effect of stirring on adsorption capacities and rates of adsorption. A 0.4 g aliquot of each of maize cob and Dowex were weighed into 25 ml solution of 100 mg/L Pb sup2+ at pH 5 in a 100 ml conical flask. Three replicates of each adsorbent were weighed to determine the effects of shaking at three different time intervals. For each adsorbent, the mixtures in the first, second and third flasks were shaken in an orbital shaker (Edmund Buhler, GmbH and Co., Germany) at 150 rpm for 30 min, 1 and 2 h, respectively. At the expiration of the respective time intervals, the mixtures were filtered using Whatman No. 1 filter paper. The filtrates were then analyzed for Pb sup2+ content. Experiments were carried out in duplicates (Kok et al., 2001; Antunnes et al., 2003; Kadirvelu and Namasivayam, 2003; Kar and Misra, 2004).

Adsorption studies on effluents

Battery and paint effluents (pH values 2.81 and 4.10 respectively at 30°C at the point of discharge) were used for the experiment. For each effluent, 0.4 g each of the adsorbents were added to 25 ml of the effluent and left standing for 2 h. At the expiration of 2 h, the mixtures were filtered and the filtrates analyzed for Pb sup2+.

Quality assurance / quality control

The following quality control measures were taken.

(i) To examine whether the filter paper used during the study adsorbed or released any metal, filtered and unfiltered samples were compared. Filtered and unfiltered distilled – deionized water were analyzed by AAS to determine if Pb sup2+ was leached from the filters. Also, samples of filtered and unfiltered 100 mg/L Pb sup2+ were examined to determine whether Pb sup2+ was retained by the filters.

(ii) Each sample was analyzed in duplicate by AAS and the mean
Table 1. Percentage removal of Pb\textsuperscript{2+} by adsorbents.

<table>
<thead>
<tr>
<th>Weight of residues (g/L)</th>
<th>Pb\textsuperscript{2+} removal from solution at equilibrium (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dowex</td>
</tr>
<tr>
<td>0.025</td>
<td>74.88a</td>
</tr>
<tr>
<td>0.05</td>
<td>80.89b</td>
</tr>
<tr>
<td>0.10</td>
<td>81.99c</td>
</tr>
<tr>
<td>0.20</td>
<td>83.74d</td>
</tr>
<tr>
<td>0.40</td>
<td>85.80e</td>
</tr>
<tr>
<td>0.60</td>
<td>86.16f</td>
</tr>
</tbody>
</table>

Figures followed by the same letter within a column do not differ significantly according to DMRT at 5% level of probability.

Adsorption Kinetics

Kinetic study for adsorption was conducted at the optimal pH 5 (Kadirvelu and Namasiyam, 2003). The adsorption rate constants (K\textsubscript{ad}) were calculated using Lagergren’s equation expressed mathematically as:

\[
\log (Q_e - Q) = \log Q_e - (K_{ad} \times 2.303)/t
\]

where \( Q \) = amount of Pb\textsuperscript{2+} adsorbed in mg/g at time \( t \), \( Q_e \) = amount of Pb\textsuperscript{2+} adsorbed in mg/g at equilibrium time, and \( K_{ad} \) = rate constant of adsorption (1/min).

Adsorption isotherms

Freundlich isotherm was used to describe adsorption pattern. The model assumes multiple layers at the adsorbent surface and that adsorption will increase as long as concentration increases. The model is described by the equation

\[
Q_e = K_n C_e^{1/n}
\]

and can be linearized as

\[
\log Q_e = \log K + 1/n \log C_e
\]

where \( C_e \) = Equilibrium concentration of Pb\textsuperscript{2+} in solution (mg/L), \( Q_e \) = Amount of Pb\textsuperscript{2+} adsorbed per unit weight of adsorbent at equilibrium (mg/g), \( K_n \) = Constant indicative of capacity of adsorbent (1/mg), and \( n \) is a constant indicative of the affinity of Pb\textsuperscript{2+} towards residues whose value ranges between 0 and 1.

A plot of Log \( Q_e \) against Log \( C_e \) yielding a straight line indicates a confirmation of the Freundlich’s adsorption isotherm.

Statistical analysis

Statistical tools used include descriptive statistics (mean, standard deviation), regression and correlation analysis. Duncan multiple range test was also used for means separation for statistical significance at 95% confidence level (\( p = 0.05 \)).

RESULTS AND DISCUSSION

Initial parameters for study

The initial pH values of the battery and paint effluents were 2.81 and 4.10 respectively while Pb\textsuperscript{2+} concentrations were 8.96 and 9.45 mg/L respectively at 30°C.

Capacity studies

The study established that the amount of adsorbent used is an important factor affecting Pb\textsuperscript{2+} removal from solution. Variation in adsorption capacities between the two adsorbents may be ascribed to the type and surface groups responsible for interaction with metal ions (Dakiky et al., 2002). Increases in adsorbent weight resulted in increased percentage adsorption until equilibrium was attained. Dowex adsorbed better than maize cob in Pb\textsuperscript{2+} standard solutions (Tables 1 and 6) while the converse is the case in adsorption from battery and paint effluents (Table 6). There were significant differences in percentage adsorption of Pb\textsuperscript{2+} for different adsorbent weights (Table 1). Similar results have been reported by Shukla and Pai (2005) who used coir, jute, sawdust and groundnut shells for Pb\textsuperscript{2+} removal from aqueous solutions. Normanbhay and Palanisamy (2005) used chitosan coated oil palm shell to remove Cr\textsuperscript{3+} and Cr\textsuperscript{6+} from aqueous solutions while Mahvi et al. (2005) used tea waste for the removal of Pb\textsuperscript{2+}, Cd\textsuperscript{2+} and Ni\textsuperscript{2+} from industrial wastewaters. They explained that increasing adsorption with adsorbent weight can be attributed to concentration was calculated. The relative standard deviation (RSD) for each sample was calculated as the standard deviation of the samples divided by the average of the samples. The value was multiplied by 100 to put it on a percent basis (Brown et al., 2000).
Table 2. Percentage removal of \(\text{Pb}^{2+}\) by adsorbents at different time intervals.

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>(\text{Pb}^{2+}) removal from solution at equilibrium (mg/L)</th>
<th>Dowex</th>
<th>Maize cob</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>75.86a</td>
<td>21.60a</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>76.42b</td>
<td>42.70b</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>84.77c</td>
<td>53.44c</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>85.01d</td>
<td>77.90d</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>85.15e</td>
<td>78.90e</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>91.95f</td>
<td>78.20f</td>
<td></td>
</tr>
</tbody>
</table>

Figures followed by the same letter within a column do not differ significantly according to DMRT at 5% level of probability.

Table 3. Percentage removal of \(\text{Pb}^{2+}\) at equilibrium at different pH values.

<table>
<thead>
<tr>
<th>pH values</th>
<th>(\text{Pb}^{2+}) removal from solution by adsorbents (mg/L)</th>
<th>Dowex</th>
<th>Maize cob</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>39.09a</td>
<td>41.50a</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>52.38b</td>
<td>56.25b</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>59.17c</td>
<td>60.45c</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>67.99d</td>
<td>72.55d</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>69.41e</td>
<td>76.50e</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>69.97f</td>
<td>77.85f</td>
<td></td>
</tr>
</tbody>
</table>

Figures followed by the same letter within a column do not differ significantly according to DMRT at 5% level of probability.

**Figure 1.** Percentage adsorption of adsorbents with varying pH values.

The rate of adsorption is an important factor in wastewater remediation; it is therefore important to establish the time dependence of contaminant capture under process conditions (Brown et al., 2000). Values of lead concentration reduction obtained in batch contact time studies are presented in Table 2. Adsorption differed significantly for both adsorbents at different time intervals (Table 2) and optimum adsorption was obtained at 2 h contact time. The result is consistent with Ilhan et al. (2004) who also reported 2 h equilibrium time for \(\text{Pb}^{2+}\) when *Staphylococcus saprophyticus* was used as adsorbent. Adsorption rate constants \((7.58 \times 10^{-2} \text{ and } 7.26 \times 10^{-2})\) for Dowex and maize cob respectively were comparable to those from previous studies (Kadirvelu and Namasivayam, 2003; Ilhan et al., 2004; Shukla and Pai, 2005).

**Effects of contact time**

The rate of adsorption is an important factor in wastewater remediation; it is therefore important to establish the time dependence of contaminant capture under process conditions (Brown et al., 2000). Values of lead concentration reduction obtained in batch contact time studies are presented in Table 2. Adsorption differed significantly for both adsorbents at different time intervals (Table 2) and optimum adsorption was obtained at 2 h contact time. The result is consistent with Ilhan et al. (2004) who also reported 2 h equilibrium time for \(\text{Pb}^{2+}\) when *Staphylococcus saprophyticus* was used as adsorbent. Adsorption rate constants \((7.58 \times 10^{-2} \text{ and } 7.26 \times 10^{-2})\) for Dowex and maize cob respectively were comparable to those from previous studies (Kadirvelu and Namasivayam, 2003; Ilhan et al., 2004; Shukla and Pai, 2005).

**Effect of pH on percentage adsorption**

The pH of solution has a significant impact on metal uptake since it determines the surface charge of adsorbent and the degree of ionization and speciation of adsorbate (Cho et al., 2005). Percentage adsorption was highest for both adsorbents at the highest pH but equilibrium was attained at pH 6 as previously reported (Akhtar et al., 2004; Aziz et al., 2008). There were significant differences in adsorption capacities of both adsorbents at different pH values at a confidence limit of 95% (Table 3 and Figure 1).

Enhanced adsorption with increasing pH from 2 to 8 suggests that adsorbents’ surfaces become more negatively charged. This resulted in a more favourable electrostatic attraction forces and so, enhanced cationic metal ion adsorption as pH increased (Cho et al., 2005;
Table 4. Percentage Pb\(^{2+}\) removal at different concentrations by adsorbents.

<table>
<thead>
<tr>
<th>Pb(^{2+}) concentration (mg/L)</th>
<th>Removal of Pb(^{2+}) from solution at equilibrium (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dowex</td>
</tr>
<tr>
<td>20</td>
<td>51.40a</td>
</tr>
<tr>
<td>40</td>
<td>67.18b</td>
</tr>
<tr>
<td>100</td>
<td>85.77c</td>
</tr>
<tr>
<td>200</td>
<td>90.40d</td>
</tr>
<tr>
<td>400</td>
<td>93.71e</td>
</tr>
<tr>
<td>600</td>
<td>95.50f</td>
</tr>
</tbody>
</table>

Figures followed by the same letter within a column do not differ significantly according to DMRT at 5% level of probability.

**Effect of lead concentration on percentage adsorption**

The effects of initial Pb\(^{2+}\) concentration on percentage adsorption by adsorbents are presented in Table 4. Significant differences occurred in adsorption at 95% confidence limit for both adsorbents and at different Pb\(^{2+}\) concentrations. However, adsorption tends to be constant with increasing Pb\(^{2+}\) concentration for maize cob while it increased steadily for Dowex. The results are consistent with those of Horsfall and Spiff (2004) and Goksungur et al. (2003) who reported that initial metal ion concentration may not have any significant increase in adsorption. Experimental data fitted well into Freundlich’s Isotherm model with very high positive coefficients of determination for both adsorbents (Figures 2 and 3). Significant adsorption may therefore take place even at high metal concentrations suggesting multilayer sorption. Hence, adsorption would be random, due to existence of a distribution of energetically different active sites (Dakiky et al., 2002).

**Effects of shaking period**

Effects of shaking at 150 rpm at different time intervals on percentage adsorption of Pb\(^{2+}\) by different adsorbents are presented in Table 5. In this study, percentage adsorption was greatly enhanced by shaking except maize cob at 60 min which may be due to experimental error. The equilibrium value was attained at 30 min for Dowex while maize cob achieved the optimum in 2 h (Table 5). For both adsorbents, percentage adsorption of Pb\(^{2+}\) was enhanced by shaking both in standard solution and in the effluents (Table 6). Initial Pb\(^{2+}\) concentrations in standard solution, battery and paint effluents were 100, 8.96 and 9.45 mg/L respectively. In battery effluent, 100% adsorption was achieved with maize cob in both shaken and unshaken experiments. Also in paint effluent, maximum adsorption was achieved for maize cob under vigorous shaking. Increased percentage adsorption was more pronounced in battery and paint effluents than in 100 mg/L standard solution of Pb\(^{2+}\) in both shaken and unshaken experiments.

Various scientists have also reported trends of increased percentage adsorption as reported in this study (Engl and Kunz, 1995; Antunnes et al., 2003; Kadirvelu, 2008). In contrast, decreases in Pb\(^{2+}\) adsorption at low pH values is due to an increase in competition for adsorption sites by H\(^+\).

\[ y = 0.9981x - 1.2014 \]
\[ R^2 = 1 \]
Table 5. Percentage adsorption of Pb$^{2+}$ onto adsorbents after shaking at different time intervals (Mean ± SD) n = 2.

<table>
<thead>
<tr>
<th>Residue</th>
<th>Shaking period (min)</th>
<th>Residual Pb$^{2+}$ (mg/L)</th>
<th>% Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dowex</td>
<td>30</td>
<td>9.59±3.67</td>
<td>90.41*</td>
</tr>
<tr>
<td>Dowex</td>
<td>60</td>
<td>9.32±1.29</td>
<td>90.68</td>
</tr>
<tr>
<td>Dowex</td>
<td>120</td>
<td>9.08±3.55</td>
<td>90.92</td>
</tr>
<tr>
<td>Maize cob</td>
<td>30</td>
<td>30.20±3.03</td>
<td>69.80</td>
</tr>
<tr>
<td>Maize cob</td>
<td>60</td>
<td>35.53±4.37</td>
<td>64.47</td>
</tr>
<tr>
<td>Maize cob</td>
<td>120</td>
<td>13.10±4.57</td>
<td>86.90*</td>
</tr>
</tbody>
</table>

Note: Asterisked values are the equilibrium percentage adsorption for the respective adsorbents.

Table 6. Effect of shaking on percentage adsorption of Pb$^{2+}$ in 100 mg/L standard solution and effluents at equilibrium.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pb$^{2+}$ Standard solution</th>
<th>Effluents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shaken</td>
<td>Unshaken</td>
</tr>
<tr>
<td>Dowex</td>
<td>88.92</td>
<td>85.77</td>
</tr>
<tr>
<td>Maize</td>
<td>86.90</td>
<td>77.90</td>
</tr>
</tbody>
</table>

and Namasivayam, 2003; Kar and Misra, 2004). In explaining this phenomenon, Engl and Kunz (1995) showed that Pb$^{2+}$ suppresses the removal of other ions from mixed solutions; this may partly be explained by the greater stability constant of Pb$^{2+}$ when bound to the surface ligands, for which other metals compete, and partly, by the smaller hydration envelope that enables Pb$^{2+}$ to diffuse more rapidly in solution.

**Conclusion**

Two adsorbents maize (Z. mays) cob and dowex (a synthetic adsorbent) were used to bind Pb$^{2+}$ from standard aqueous solutions. Effects of adsorbent weight, Pb$^{2+}$ concentration, contact time and pH were assessed to determine equilibrium conditions for adsorption. Adsorption rate constant for both adsorbents were comparable to those of previous studies and both fitted well into Freundlich’s adsorption isotherm. The implication of this is that adsorption processes occurred on non-uniform surfaces; hence, adsorbents were multi-layered such that percentage adsorption will increase as long as concentration increases. Comparative assessment of shaken and unshaken experiments revealed that shaking enhanced percentage adsorption by both adsorbents except maize cob at 60 min.

Since maize cob have the potential to remove Pb$^{2+}$ from aqueous solutions and industrial effluents, it implies that it may also decontaminate wastewaters containing other divalent metal ions such as Zn$^{2+}$, Cd$^{2+}$, amongst others. There is therefore the need for more extensive research on possibility of removing such metals using other crop residues since typical wastewaters contain mixed metal ions. This may increase the extent of use and applicability of the residues in wastewater remediation.

**REFERENCES**


