This study was carried out to evaluate the efficiency of metals (Cu, Fe, Pb, Cr and Cd) removal from mixed metal ions solution using coconut husk as adsorbent. The effects of varying contact time, initial metal ion concentration, adsorbent dose and pH on adsorption process of these metals were studied using synthetically prepared wastewater. The percentage removal of metals increased with increasing weight (0.4-1.2 g) in 50 ml of adsorbent dose and the observed trend was: Cr>Cu>Pb>Fe>Cd. The adsorption efficiency increased with increasing initial metal ion concentration (0.3-0.9 mg/l) and the observed trend was: Cr>Cu>Cd>Fe>Pb. Similarly, percentage removal of metal ions increased with increasing pH of the mixed metal ions solution (pH values of 2, 6 and 10). The observed trend of percentage adsorption of metals by varying pH was: Cd>Fe>Cr>Cu>Pb. The effect of contact time on the adsorption efficiency at different time intervals of 20, 40 and 60 min in mixed metal ions solution showed that the removal of tested metals was rapidly achieved during a short interval of 20 min. Generally, the study showed that coconut husk (a waste material) is a viable material for removal of metals from waste water as the percentage adsorbed varies from 95.2-98.8, 91.1-99.3 and 75.0-98.5% for Cd, Cr and Cu, respectively while the percentage removal of Fe and Pb from the waste water varies from 84.9-97.0 and 81.1-98.7%, respectively. Isothermal studies showed that the experimental data are best fitted on Langmuir model.

Key words: Batch adsorption, heavy metals, wastewater, coconut husk.

INTRODUCTION

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and their presence pose environmental-disposal problems due to their non-degradable and persistence nature. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Gupta et al., 2001). The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes stream of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage batteries industries, etc. (Goyal and Ahluwalia, 2007; Olayinka et al., 2007, 2009; Kadirvelu et al., 2001). Treatment processes for
Adsorption on low cost-adsorbent for removal of toxic metals from wastewater has been investigated extensively. These materials include thioglycolic acid modified oil-palm (Akaninwor et al., 2007), wild cocoyam biomass (Horsfall and Spiff, 2004), brewery biomass (Kim et al., 2005), sodium hydroxide modified Lalang (Imperata cylindrica) and leaf powder (Hanafiah et al., 2006). Recently, efforts have been made to use cheap and available agricultural wastes such as coconut shell, orange peel, rice husk, peanut husk and sawdust as adsorbents (Vaishnav et al., 2012) to remove heavy metals from wastewater (Abia and Igwe, 2005).

The use of the coconut shell as a biosorbent material presents strong potential due to its high content of lignin of about 35-45%, and cellulose of about 23-43% (Carrijo et al., 2002). As a result of its low cost, powder of coconut shell- Cocos nucifera is an attractive and inexpensive option for the biosorption removal of dissolved metals. Various metal-binding mechanisms are thought to be involved in the biosorption process including ion exchange, surface adsorption, chemisorption, complexation and adsorption-complexation (Pino, 2005; Matheickal et al., 1999).

Coconut shell is a material composed of several constituents, among them lignin acid and cellulose bear various polar functional groups including carboxylic and phenolic acid groups which can be involved in metal binding (Matheickal et al., 1999; Ting et al., 1991). The cellulose and lignin are biopolymers admittedly be associated to the removal of heavy metals (Gaballah and Kilbertus, 1994; Gaballah et al., 1997; Hunt, 1986). Adsorption on low cost-adsorbent for removal of toxic metals from wastewater has been investigated extensively. These materials include thioglycolic acid modified oil-palm (Akaninwor et al., 2007), wild cocoyam biomass (Horsfall and Spiff, 2004), brewery biomass (Kim et al., 2005), sodium hydroxide modified Lalang (Imperata cylindrica) and leaf powder (Hanafiah et al., 2006).

However, these studies did not involve batch adsorption process but rather single adsorption of metal ions from their aqueous solutions, although study carried out by Abdel-Ghani and El-Chaghaby (2009) involved batch adsorption process.

In this study, the use of unmodified coconut husk in the removal of metal ions from aqueous solutions through batch adsorption studies was investigated. Coconut husk which is generally considered as a waste is abundant in Nigeria and has a high sorption capacity due to its high tannin content. This study involved the examination of four variables such as pH of the solution, metal ion concentration, contact time and adsorbent loading on the removal of Cu(II), Fe(III), Cd(III), Cr(III) and Pb(II) ions from aqueous solutions, simultaneously.

MATERIALS AND METHODS

Adsorbent

Coconut (C. nucifera) shell/husk were collected from Abusoro at Okitipupa Local Government Area of Ondo State, Nigeria; sun dried for about 2-5 days before being ground into fine particles using the manual grinding machine and sieved with sifter to obtain 120 mm (micrometer mesh) finer dust particles. The finer dust particles were treated with 0.1 M HCl and was later re-introduced into an oven at a temperature of 30°C for 30 min and then preserved in a sample container for future use.

The concentrations of Cu, Cd, Fe, Cr and Pb ions in the adsorbent were determined by placing 5 g of the adsorbent in 50 ml de-ionized water for 50 min in a 50 cm long and 2 cm diameter glass column. Aliquot portions of the eluate from the pre-treatment of the organic waste were carefully decanted into 50 ml plastic bottles and analyzed for the heavy metals using Atomic Absorption Spectrophotometer (AAS) GBC Scientific with oxy-acetylene flame at temperature of about 2500°C.

Adsorption technique

A glass column was fitted with cotton wool and held firmly in a vertical position with the aid of a clamp fixed at one end to a retort stand as illustrated in Figure 1. Atmospheric pressure helped to push the sample through the organic material.

Adsorption experiment was done by measuring 50 ml of the wastewater sample and poured into a 100 ml conical flask. 5 g of the pre-treated fine particle coconut husk was added to the wastewater.

Adsorbates

The solutions of Cu, Cd, Fe, Cr and Pb metal ions were prepared from analytical grade CuSO4.5H2O, 3Cd(SO4).8H2O, FeSO4.7H2O, Cr(NO3)3.9H2O and Pb(NO3)2 respectively from BDH Chemicals Ltd, Pool England. 30 mg/L aqueous solutions (stock solutions) of these salts were prepared with de-ionized water in 250 ml volumetric flask and these stock solutions were diluted with de-ionized water to obtain the working standard solutions.

In each set of experiment, the effect of one factor was evaluated by varying this factor while keeping all other factors constants.

Adsorption experiments

Batch adsorption process was carried out at laboratory room temperature. The different factors affecting adsorption process of
the metal ions under study (Cu\(^{2+}\), Pb\(^{2+}\), Fe\(^{3+}\), Cr\(^{3+}\) and Cd\(^{2+}\)) such as contact time, concentration, adsorbent dose and pH have been studied using synthetically prepared wastewater. The sorption capacity \(q_e\) mg/g and removal efficiency \(Q\) were obtained according to the Equations 1 and 2, respectively:

\[
q_e = \frac{(C_0 - C_e)W}{V} \quad (1)
\]

\[
Q = \frac{(C_0 - C_e) \times 100\%}{C_0} \quad (2)
\]

Where \(V\) is the volume of the solution, \(W\) is the amount of adsorbent, \(C_0\) and \(C_e\) are the initial and concentration of the solution after adsorption in mg/l.

Statistical analysis

The relationship between pairs of metal adsorption at the various variables was tested using Pearson Moment Correlation Coefficient. All statistical analyses were tested using SPSS 21.00 with significance based on 95% confidence level (Ogbeibu, 2005).

RESULTS AND DISCUSSION

Effect of adsorbent dosing

The availability and accessibility of adsorption site is controlled by adsorbent dosage (Rafeah et al., 2009). The effect of mass of adsorbent loading on heavy metal removal using coconut husk was investigated by varying adsorbent loading weight from 0.4 to 1.2 g per 50 ml of mixed metal ions solutions (Appendix 1). The effect of coconut husk weight is graphically presented in Figure 2. It can easily be inferred that the percentage removal of metal ions increased with increasing weight of coconut husk. This is due to the greater availability of the exchangeable sites or surface area at higher dose of the adsorbent. This result is in agreement with previous studies on many other adsorbents (Bin et al., 2001; Ajmal et al., 1998; Abdel-Ghani and El-Chaghaby, 2009). The observed trend of percentage removal of metal ions was: Cr>Cu>Pb>Fe>Cd. Furthermore, the P-values of 0.058 and 0.090 at 95% confidence level (P>0.05) shows statistically that there was no significant correlation in adsorption pattern between Cu and Cd and that of Cu and Fe. However, there exist significant correlation in adsorption pattern between Cu and Cr and that of Cu and Pb, since P<0.05 at 95% confidence level. Similarly, there exist a significant correlation between the pairs of Cd and Fe (P<0.05) and that of Cd and Pb (P<0.05) at 95% confidence level. The same trend was observed statistically between the pairs of Fe and Cr (P<0.05) and Fe and Pb (P<0.05). However, there was no significant correlation statistically between the adsorption pattern of Cr and Pb at 95% confidence level (P>0.05).

Effect of concentration on adsorption of the metal ions

The effect of initial metal concentration on the adsorption efficiency of coconut husk is shown in Figure 3. Adsorption experiments were carried out at different initial metal ion concentrations of 0.03, 0.06 and 0.09 mg/l in mixed metal ions solution (Appendix 2). The adsorption efficiency increased with increasing initial metal ion concentration. This result is in accordance with the work of Okieimen and Onyenkpa (2000). It is generally expected that as the concentration of the adsorbate increases the metal ions removed should increase. It is believed that increase in concentration of the adsorbate bring about increase in competition of adsorbate molecule for few available binding sites on the surface of the adsorbent hence increase in the amount of metal ions removed. The observed trend of percentage removal of metal ions was: Cr>Cu>Cd>Fe>Pb. The P-values of 0.041 and 0.018 at 95% confidence level (P>0.05) shows statistically that there was significant correlation in adsorption pattern between Cu and Cd and that of Cu and Cr. However, there was no significant correlation in adsorption pattern between Cu and Fe (P<0.05). Cd shows statistically that there was significant correlation in the adsorption pattern with the rest metals (Cu, Fe, Cr and Pb) as their P<0.05. Fe also shows statistically significant correlation with Pb (P<0.05) at 95% confidence level.

Effect of hydrogen ion concentration

The pH adsorption edges of the constant concentration for Cu, Cd, Fe, Cr and Pb for coconut husk are shown in Figure 4. All experiments were carried out in the pH
values of 2, 6 and 10 (Appendix 3) where chemical precipitation is almost avoided, so that metal removal could be related to the adsorption process (Abdel-Ghani and El-Chaghaby, 2009).

The susceptibility of the system pH changes may be attributed to the nature of the ions in solution and the nature of the adsorbent used. The lower the pH, the more H⁺ ions competing with the metal ions for adsorption.

**Figure 2.** Effect of coconut loading weight on metal ion adsorption in a mixed metal ion solution.

**Figure 3.** Effect of variation in initial metal ions concentration on adsorption using coconut husk.
Effect of hydrogen ion concentration (pH) on metal ions adsorption.

sites, thus reducing their adsorption. On the other hand, the higher the pH, the less the H⁺ ions competing with metal ions for adsorption sites, thus increasing their adsorption, which explains the obtained results in Figure 4. The observed trend of percentage adsorption of metal ions was: Cd>Fe>Cr>Cu>Pb. Furthermore, the P<0.05 at 95% confidence level shows statistically that there was significant correlation in adsorption pattern between Cu and Cd; Cu and Fe; and Cu and Pb, respectively. Similar trend of adsorption pattern statistically was observed between Cd and Cr (P<0.05) and Cd and Pb (P<0.05).

Effect of contact time

The effect of contact time on the adsorption efficiency is shown in Figure 5. Adsorption experiments were carried out at different time intervals: 20, 40 and 60 min in mixed metal ions (Appendix 4). It was observed that removal of tested metals was rapidly achieved, within a short period of 20 min. Adsorption of Cd and Cr ions attained maximum within 20 min while that of Cu was within 40 min. Adsorption of Fe and Pb increases with increase in contact time. Generally, the observed trend of metal removal was: Pb>Cu>Cr>Fe>Cd. Previous results revealed that removal of all tested metals was rapidly removed within a short period of 30 min (Olayinka et al., 2009). The effect of contact time on adsorption process of metal ions from wastewaters were studied by many authors (Dakiky et al., 2002; Saeed et al., 2005; Abdel-Ghani et al., 2007a; Abdel-Ghani et al., 2007b). The results indicated that the equilibrium time was dependent on the nature of the adsorbent and on metal ions concentration. Furthermore, the P<0.05 at 95% confidence level shows statistically that there was significant correlation in adsorption pattern between Cu and the rest metals (Cd, Fe, Cr and Pb, respectively). Similarly, Cd exhibited statistically significant correlation with Fe (P<0.05) but there was no significant correlation with Pb (P>0.05). However, there exist statistically significant correlation in adsorption pattern between Fe and Cr (P<0.05) and Pb (P<0.05). The P>0.05 shows statistically that there was no significant correlation between the adsorption pattern of Cr and Pb.

Isothermal studies

The analysis of equilibrium data for the adsorption of Cd, Cr, Cu, Fe and Pb on coconut husk was done using the Langmuir and Freundlich isotherm model as shown in Tables 1 and 2, respectively. The extremely high R² values provided by the Langmuir isotherm suggest that the data best fitted the Langmuir isotherm given by the equation:

\[
qe = \frac{v}{m(Co - Ce)}.
\]
Table 1. Values of Langmuir Isotherm constants for sorption of Cd, Cr, Cu, Fe and Pb metal ions.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>$q_{max}$ (mg/g)</th>
<th>$K_L$ (l/mg)</th>
<th>$R_L=1/(1+K_L C_0)$</th>
<th>$R^2$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.00010</td>
<td>786.1</td>
<td>0.041</td>
<td>0.965</td>
</tr>
<tr>
<td>Cd</td>
<td>0.00010</td>
<td>610.02</td>
<td>0.051</td>
<td>0.992</td>
</tr>
<tr>
<td>Fe</td>
<td>0.00009</td>
<td>118.4</td>
<td>0.22</td>
<td>0.919</td>
</tr>
<tr>
<td>Cr</td>
<td>0.00031</td>
<td>1355.00</td>
<td>0.024</td>
<td>0.835</td>
</tr>
<tr>
<td>Pb</td>
<td>0.00039</td>
<td>38.44</td>
<td>0.46</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 2. Values of Freundlich Isotherm constants for sorption of Cd, Cr, Cu, Fe and Pb metal ions.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>$K_F$ (mg/l)</th>
<th>$\frac{1}{n}$</th>
<th>N</th>
<th>$R^2$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.4E-6</td>
<td>0.810</td>
<td>1.23</td>
<td>0.148</td>
</tr>
<tr>
<td>Cd</td>
<td>1.24E-6</td>
<td>1.047</td>
<td>0.96</td>
<td>0.783</td>
</tr>
<tr>
<td>Fe</td>
<td>3.7E-7</td>
<td>1.603</td>
<td>0.62</td>
<td>0.346</td>
</tr>
<tr>
<td>Cr</td>
<td>2.0E-5</td>
<td>0.585</td>
<td>1.709</td>
<td>0.729</td>
</tr>
<tr>
<td>Pb</td>
<td>7.96</td>
<td>2.253</td>
<td>0.44</td>
<td>0.974</td>
</tr>
</tbody>
</table>

Where $C_0$ (mg/l) and $C_e$ (mg/l) are initial and equilibrium concentration of adsorbate solution respectively.

The Langmuir isotherm equation is written as:

$$q_e = \frac{q_{max} K_L C_0}{1 + K_L C_0}$$

$q_{max}$ (mg/g) is the maximum adsorption capacity upon complete saturation of the adsorbent surface, $K_L$ (dm$^3$/g) is a constant related to the adsorption/desorption energy.

The equation above can be rearranged to form the Scatchard regression:

$$\frac{q_e}{C_e} = q_{max} K_L - K_L q_e$$

A plot of $\frac{q_e}{C_e}$ versus $q_e$ yields a slope $-K_L$ and intercept $q_{max} K_L$.

The isotherm constants were determined from the respective plots, and are presented in Table 1. Regression values ($R^2$) presented in Table 1; indicate that the adsorption data for Cd, Cr, Cu, Fe and Pb metal ion removal fitted well the Langmuir isotherm.

Conclusion

This study was carried out to evaluate the efficiency of metal removal from mixed metal ions solution using...
coconut husk as adsorbent. Contact time, initial metal ion concentration, adsorbent dose and pH as factors that affect adsorption process of metals were studied using synthetically prepared wastewater. The percentage removal of metals increased with increasing weight of coconut husk and the observed trend of percentage removal of metal ions was: Cr>Cu>Pb>Fe>Cd. The adsorption efficiency increased with increasing initial metal ion concentration and the observed trend of percentage removal of metal ions was: Cr>Cu>Cd>Fe>Pb, while percentage removal of metal ions increased with increasing pH and the observed trend of percentage adsorption of metal ions was: Cd>Fe>Cr>Cu>Pb. The effect of contact time on the adsorption efficiency at different time intervals reveals that the removal of tested metals was rapidly achieved during a short period of 20 min. Generally, the study revealed that coconut husk (a waste material) is a viable material for removal of metals from waste water and therefore could be applied in large scale industrial effluents replete with heavy metals. Isothermal studies showed that the experimental data are best fitted on Langmuir model.

**Conflict of Interests**

The author(s) have not declared any conflict of interests.

**REFERENCES**


Appendix 1. Percentage removal (%) of metal ion from synthetic wastewater by varying adsorption weight.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Cu</th>
<th>Cd</th>
<th>Fe</th>
<th>Cr</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 g</td>
<td>65.80</td>
<td>70.03</td>
<td>71.47</td>
<td>71.83</td>
<td>68.10</td>
</tr>
<tr>
<td>0.8 g</td>
<td>67.03</td>
<td>75.97</td>
<td>91.13</td>
<td>83.77</td>
<td>80.03</td>
</tr>
<tr>
<td>1.2 g</td>
<td>98.53</td>
<td>85.17</td>
<td>94.70</td>
<td>98.93</td>
<td>95.20</td>
</tr>
</tbody>
</table>

Appendix 2. Percentage removal (%) of metal ion from synthetic wastewater by varying molar concentration.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Cu</th>
<th>Cd</th>
<th>Fe</th>
<th>Cr</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03 M</td>
<td>92.27</td>
<td>73.27</td>
<td>66.63</td>
<td>80.37</td>
<td>71.40</td>
</tr>
<tr>
<td>0.06 M</td>
<td>96.47</td>
<td>96.07</td>
<td>75.23</td>
<td>87.43</td>
<td>77.03</td>
</tr>
<tr>
<td>0.09 M</td>
<td>98.33</td>
<td>97.83</td>
<td>90.47</td>
<td>99.30</td>
<td>81.10</td>
</tr>
</tbody>
</table>

Appendix 3. Percentage removal (%) of metal ion from synthetic wastewater by varying pH.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Cu</th>
<th>Cd</th>
<th>Fe</th>
<th>Cr</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>66.40</td>
<td>72.53</td>
<td>78.70</td>
<td>77.03</td>
<td>71.17</td>
</tr>
<tr>
<td>pH 6</td>
<td>80.47</td>
<td>82.03</td>
<td>84.93</td>
<td>86.37</td>
<td>74.43</td>
</tr>
<tr>
<td>pH 10</td>
<td>85.13</td>
<td>98.83</td>
<td>97.03</td>
<td>91.10</td>
<td>81.90</td>
</tr>
</tbody>
</table>

Appendix 4. Percentage removal (%) of metal ion from synthetic wastewater by varying contact time.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Cu</th>
<th>Cd</th>
<th>Fe</th>
<th>Cr</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 Min</td>
<td>82.77</td>
<td>74.90</td>
<td>73.30</td>
<td>90.73</td>
<td>68.17</td>
</tr>
<tr>
<td>40 Min</td>
<td>96.57</td>
<td>75.50</td>
<td>75.30</td>
<td>92.23</td>
<td>81.90</td>
</tr>
<tr>
<td>60 Min</td>
<td>97.10</td>
<td>75.60</td>
<td>84.93</td>
<td>93.27</td>
<td>98.67</td>
</tr>
</tbody>
</table>