MULTIPLE ADSORPTION OF HEAVY METAL IONS IN AQUEOUS SOLUTION USING ACTIVATED CARBON FROM NIGERIAN BAMBOO

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Abstract
Batch adsorption of different heavy metal ions (Nickel, Copper, Zinc, Lead, Cadmium and Chromium) in aqueous solution using activated carbon from Nigerian bamboo was studied. The bamboo was cut, washed and dried. It was carbonized between 300°C - 450°C, and activated at 800°C using nitric acid. The bulk density, iodine number, Benzene adsorption, methylene adsorption, and ash content of the activated carbon produced compared well with commercial carbons. Multiple adsorption of these metals in same aqueous solution using bamboo carbon showed that adsorption capacity is in the order Pb>Cd>Cu>Zn>Ni>Cr which showed that these metal ions can be adsorbed selectively by Nigerian bamboo activated carbon. The order of adsorption is related to the maximum adsorption of lead, cadmium, copper on bamboo was found to be in the order of ionic radius of the heavy metals used. Therefore this study demonstrates that bamboo can serve as a good source of activated carbon with multiple metal ions – removing potentials and may serve as a better replacement for commercial activated carbons in applications that warrant their use. However, it will also contribute to the search for less expensive adsorbents and their utilization possibilities for the elimination of heavy metal ions from industrial waste water.

Key Words: multiple adsorption, heavy metals, Nigerian bamboo, Activated Carbon,

1. INTRODUCTION

In recent years, the need for safe and economical methods for the elimination of heavy metals from refinery waste waters necessitated research interest towards the production of low cost commercially available activated carbon. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products. Heavy metals such as Chromium, Cadmium, Lead, Copper, Zinc and Nickel often found in refinery waste waters are carcinogenic or toxic to the environment (Kocasoy and Sahin, 2007). The low cost agricultural waste-by-products such as sugarcane bagasse, rice husk, sawdust, coconut husk, oil palm shell, Neem bark, Zeolite-based oil shale ash etc used for the elimination of heavy metals from waste water have been investigated by various researchers (Nasim et al., 2004, Panida and Pisin, 2010, Wei-Wei et al., 2013, Ademiluyi and Ujile 2013). Most of the previous works reported are on single, double, and triple metal ion adsorption. Although other works, carried out by Kermit, et al.,(2005) and Myroslav et al., (2006), using activated carbon made from peanut shells and; raw and pretreated clinoptilolite showed that selective metal ion adsorption of copper, lead, cadmium, zinc and nickel is possible in same aqueous solution. Uzun and Guzel (2000) also observed that the rate of uptake of Cu++, Mn++, Fe++ and Ni++using three adsorbents (Chitosan, Agar and a commercial carbon, Merck 2514) are different and concluded that an adsorbent that adsorb one adsorbate may not be able to adsorb another adsorbate effectively. In the work of Bassam et al., (2012), the adsorption capacity of Cd(II), Ni(II), Zn(II) onto geopolymers decreases with competition in a similar manner to the adsorption of metal ions onto zeolite. However, the adsorption of Cu(II) onto geopolymers increases with competition like adsorption of metal ions onto kaolinite hence the need to study the multiple adsorption of these metal ions often found in refinery waste water. The review from previous works carried out on bamboo activated carbon showed that equilibrium study on multiple batch adsorption of different heavy metal ions from aqueous solution using activated carbon from Nigerian Bamboo is yet to be investigated for these six metals i.e. Chromium, Cadmium, Lead, Copper, Zinc and Nickel, often found in refinery waste waters. Therefore, the objectives of this research is to investigate the multiple and competitive adsorption of these metals in aqueous solution using activated carbon from Nigerian Bamboo and develop empirical models that can be used to predict the sorption process.

2. MATERIALS AND METHODS

2.1 Materials
The materials used for this study are as follows: Granular activated carbon produced from Nigerian waste Bamboo, distilled water, Nitric acid, metal salts of Nickel, Copper, Zinc, Cadmium, Lead and Chromium, Methylene Blue, Sodium Thiosulphate and Iodine solution (for
characterization of carbon). Refinery waste waters collected after treatment to analyze heavy metal ions presence. Other equipments and apparatus used for the research are: An analytical weighing Balance, pyrolyzer with condenser, Electric burner, Measuring cylinder, Heating mantle, Desiccators, Crucibles, Funnels and filter paper, Digital weighing Balance, Mortar and pestle, pH meter, Spatula, Burette and retort stand, Beakers, conical flasks, stirrer Muffle finance, Set of sieves (1.18mm, 600μm, 300μm, 150μm, 75μm), Cutting machine and oven, Atomic Absorption Spectrophotometer (AAS).

2.2 Methods

2.2.1 Preparation of Nigerian Bamboo Samples

The Nigerian Bamboo was cut into small sizes of about 2cm long with a cutting machine. After the cutting, pieces of bamboo were washed thoroughly with distilled water to remove all the adherent extraneous matter. The bamboo was then dried in the oven.

2.2.2 Carbonization Process

2 kg of Bamboo pieces were weighed into a reactor. The Bamboo was pyrolysed between (300 -450 °C) in the absence of air for two hours, 30 minutes (Ademiluyi et al., 2007). The distillate formed during the pyrolysis was collected by the receiver connected to a condenser. The charred material was cooled at room temperature before discharging it into container.

2.2.3 Chemical Activation

The carbonated material was crushed. The crushed sample was screened using 1.18mm sieve in order to get a uniform size of the particle. 100 g of carbonized bamboo was carefully weighed and put in beaker containing 150cm³ of Nitric acid. The solution was stirred until the mixture formed a paste. The paste was allowed to pass through an oven in order to reduce the moisture content. The crucible was then transferred into a muffle furnace where it was heated for 1hour at a temperature of 800 °C in the absence of air so as to increase the surface area to volume ratio of the sample for proper adsorption. After heating, it was cooled at room temperature and was washed with distilled water until the pH value was approximately 7, showing no trace of nitric acid. After washing, the activated carbon was then dried and the final product is kept in an air tight containers. The same procedure was repeated using different concentrations of Nitric acid (0.025M - 0.5M). Nitric acid was found to be the best for metal ion adsorption and so was used as previously reported by Ademiluyi and David-West, 2012.

2.3 Characterization of Activated Carbon Produced

The characterization of the activated carbon involves the determination of properties such as bulk density, pore volume, percentage burnt off, moisture content, ash content, particle size, benzene adsorption, methylene blue and iodine number. (Ademiluyi et al., 2007).

2.4 Determination of Adsorption Capacity

Six metal ions (Cd²⁺, Ni²⁺, Pb²⁺, Cr³⁺, Cu²⁺ and Zn²⁺) often found in industrial waste waters especially refineries were used for this study. Different concentrations of these heavy metals ions in solution were prepared. Batch adsorption of the six metal ions onto bamboo activated carbon was carried out in the same aqueous solution for the different concentrations of these heavy metals ions in solution i.e. 100ml of the six metal ions in solution : 1g of activated carbon. Each sample was stirred, and adsorption was carried out for 30, 45, 90, 120, 240 and 990 minutes till equilibration. After each time interval the sample was filtered with filter paper to remove any carbon particles. This process was repeated for different concentrations of these heavy metals ions in solution. 5 ml of the resulting filtrate from each sample was diluted with 50ml of 2 % nitric acid and metals ions in filtrate after digestion were analyzed using Atomic Absorption Spectrophotometer (AAS).

3.5 Metal Uptake

The amount of metal adsorbed per unit weight of adsorbent, Qe (mg/g), was calculated from equation 1. (Kannan and Veemaraj, 2009)

\[ Q_e = \frac{(C_o - C_e) V}{M} \]

where;

- \( C_o \) = The initial metal concentration in liquid phase (mgL⁻¹)
- \( C_e \) = The liquid phase metal concentration at equilibrium (mg L⁻¹)
- \( V \) = The volume of metal solution used (L)
- \( M \) = The mass of adsorbent used (g)

3. RESULTS AND DISCUSSION

3.1 Characterization of Activated Carbon from Bamboo

The work of Ademiluyi and David-West (2012) on effect of chemical activation on the adsorption of heavy metals using activated carbon from waste materials revealed that waste Bamboo activated with HNO₃, effectively remove metal ions from waste streams and in different metal recovery processes than other activating agent. Hence different concentration of Nitric acid was initially prepared and used for activation in this study. Iodine Number is a measure of micro-porous structures of the activated carbon which shows the degree of porosity of Bamboo carbon and Benzene adsorption is a measure of meso-pore content of activated carbon. The higher the Benzene adsorption capacity, the higher the degree of adsorption hence these two parameters were used to determine the best concentration of Nitric acid to be used for activation. Fig. 1 shows a plot of Iodine Number and Benzene adsorption capacity of the activated carbon produced against concentration of activating agent. The Iodine number of carbon produced was highest at 0.1 M concentration of Nitric acid. Also Benzene adsorption
capacity plotted against different concentration of activating agent in Figure 1, showed that as concentration of the activating agent used to activate the carbon increased, the amount of benzene adsorbed also increased to a maximum value at 0.1 M of Nitric acid. Benzene adsorption capacity decreased to a minimum value at Nitric acid concentration of 0.025 M. Hence the activated carbon used for the adsorption of the heavy metal ions in this study was activated using 0.1M Nitric acid.

Table 1 shows the characterization of activated carbon of the Nigerian Bamboo used for the batch adsorption of Nickel, Copper, Zinc, Lead, Cadmium, and Chromium ions in solution compared with reference activated carbon. Moderate bulk density, favours better adsorption and from Table 1, the bulk density falls within the reference standard. The Methylene Blue adsorptive capacity which is a measure of meso-pore content of the activated carbon also falls within the reference standard. The higher the Iodine Number, (a measure of activity level and the micro pore content of the activated carbon; higher number indicates higher degree of activation) the higher the degree of adsorption. The ash content obtained after activation, compares favourably with reference activated carbon. Adsorption is more favored when ash content is neither too high nor too low.

<table>
<thead>
<tr>
<th>S/No.</th>
<th>Parameters</th>
<th>Units</th>
<th>Locally made Bamboo activated carbon</th>
<th>Reference Standards (Activated Carbon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Bulk Density</td>
<td>g/cm³</td>
<td>0.458</td>
<td>0.2-0.6 Long and Criscione (2003)</td>
</tr>
<tr>
<td>2.</td>
<td>Iodine number</td>
<td>g of Iodine/kg of carbon</td>
<td>1,160</td>
<td>500-1200 Long and Criscione (2003)</td>
</tr>
<tr>
<td>4.</td>
<td>Methylene-Blue adsorptive capacity</td>
<td>mg/g</td>
<td>941.325</td>
<td>900-1100 Wikipedia (2014)</td>
</tr>
<tr>
<td>5.</td>
<td>Benzene adsorptive capacity</td>
<td>mg/g</td>
<td>148.9</td>
<td>129 Ademiluyi et al. (2007)</td>
</tr>
</tbody>
</table>

3.2 Concentration of Metal ions (mg/L) in Refinery Waste Water Before and After Adsorption Compared with WHO Standard.

Refinery waste water used for this research was obtained after the treatment plant of the refinery and still has a conductivity of 82 μS. Hence the metal ions in the waste water from the refinery was analyzed before and after treatment with bamboo activated carbon. In Fig 2, the concentration of metal ions mg/L was plotted against metal ions in refinery waste water before and after adsorption along with the World Health Organization’s (WHO) standard on the maximum allowable limit of these metal ions in waste water.

The concentration of these heavy metal ions was high before adsorption from the treated refinery waste water as shown in Figure 2. Lead, Nickel and Cadmium in refinery waste water...
before adsorption was higher than the quantity required by WHO while the concentrations of Chromium, Copper and Zinc in refinery waste water before adsorption were below the concentration required by World Health Organization. The concentrations of metal ions after adsorption with bamboo carbon reduced drastically. In fact Copper and Chromium were adsorbed completely, which shows the effectiveness of activated carbon from Nigerian Bamboo. The result was compared with WHO standards as shown in Fig. 2 and this result also showed that Bamboo activated carbon adsorb metal ions in same aqueous solution competitively or selectively. After adsorption with Bamboo activated carbon, the amount of metal ions available was too small to study the adsorption until equilibrium is reached because the refinery wastewater was already treated. Hence metallic salts containing these metal ions were used for the study.

3.3 Quantity of Adsorbate adsorbed at equilibrium against equilibrium concentration

Fig. 3 shows the quantity of adsorbate adsorbed at equilibrium against equilibrium concentration. The quantity of heavy metal ions adsorbed increased with increase in concentration of adsorbate. Since the activated carbon used is a micro porous adsorbent, heavy metals penetrate easily into these pores as the concentration of these metal ions increased. The amount adsorbed also increased until the pores were saturated where the adsorbates can no longer be adsorbed at the pores. Similar behavior was observed by Zacaria, et al., (2002) during the study of the adsorption of several metal ions onto a low-cost biosorbent. As shown in Fig. 3 high amount of Lead, Cadmium, Copper and were adsorbed at the same time than Nickel , Zinc, and Chromium. This is an indication that Bamboo activated carbon has more affinity for some metals than others.

3.4 Rate of Multiple Adsorption of Heavy Metal ions using Activated Carbon from Bamboo in aqueous solutions of Different Concentrations.

Fig. 4 shows the amount of heavy metal ions adsorbed (Q) in mg/g of carbon at different adsorption times for the different metal ions in aqueous solution using 166 mg/L of each metal ions from the metallic salts in aqueous solution. The amount of heavy metal ions adsorbed differ for different metal ions in solution. Each of the heavy metal ions exhibited some level of desorption before attainment of equilibrium at about 240 minutes. At the initial stage, the rate of removal of the metal ions was higher, due to the availability of more active sites on the surface of the carbon and became slower at later stages of contact time, due to the decreased or lesser number of active sites. Similar results have been reported for the removal of dyes organic acids and metal ions by (Kannan and Veemaraj, 2009).

This is an indication that the multiple adsorption of heavy metal ions is time dependent. The uptake rate is controlled by the rate at which the adsorbate is transported from exterior to the interior sites of the adsorbent particles. Fig 4 also shows how these metal ions are adsorbed selectively at same time interval. The amount of metal ions adsorbed also differs though the metallic salts added before adsorption was the same. Using same concentration of adsorbate, Lead, Cadmium and Copper are more adsorbed than Zinc, Nickel and Chromium, i.e. Pb>Cd>Cu>Zn>Ni>Cr. This shows that Bamboo can be employed effectively in batch adsorption of different heavy metal ions in aqueous solution.

The work of Ingmar (2010) on hydrated metal ions in aqueous solution shows that the M–O bonds are mainly of electrostatic character, the coordination number of the hydrated metal ions is expected to be determined by the ratio of the ionic radius of the metal ion and the radius of the water oxygen atom; the size of the water oxygen atom at coordination to metal ions has been determined to be 1.34
Å. It is therefore expected that metal ions with an ionic radius smaller than 0.55 Å is expected to be tetrahedral, metal ions with an ionic radius in the range 0.55–0.98 Å are expected to be octahedral, while metal ions with an ionic radius larger than 0.98 Å are expected to be eight-coordinate or have an even higher coordination number. This principle can be used to explain why Lead and Cadmium ions were more adsorbed by Bamboo activated carbon than other metals.

Table 2. Overview of Mean Bond Distance, Ionic Radius, of the Hydrated Metal Ions Adsorbed.

<table>
<thead>
<tr>
<th>S/No</th>
<th>Aqua complex of metal ions adsorbed</th>
<th>M–O distance* Å</th>
<th>Ionic /Å*</th>
<th>Amount of metal ions in 166mg of metallic salt/ liter of aqueous solution before adsorption (mg/L) from present study</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pb(H₂O)₆²⁺</td>
<td>2.54</td>
<td>1.19</td>
<td>124.17</td>
</tr>
<tr>
<td>2</td>
<td>Cd(H₂O)₆³⁺</td>
<td>2.30</td>
<td>0.95</td>
<td>89.83</td>
</tr>
<tr>
<td>3</td>
<td>Cu(H₂O)₆²⁺</td>
<td>1.96-2.28</td>
<td>0.73</td>
<td>78.83</td>
</tr>
<tr>
<td>4</td>
<td>Zn(H₂O)₆²⁺</td>
<td>2.08</td>
<td>0.74</td>
<td>67.50</td>
</tr>
<tr>
<td>5</td>
<td>Ni(H₂O)₆²⁺</td>
<td>2.055</td>
<td>0.69</td>
<td>63.16</td>
</tr>
<tr>
<td>6</td>
<td>Cr(H₂O)₆³⁺</td>
<td>1.96</td>
<td>0.615</td>
<td>54.66</td>
</tr>
</tbody>
</table>

*Ingumar (2010) where M–O is metal ions mean bond distance and O– oxygen in water

As reported by Ingmar (2010), the expected coordination figure for four-coordination is therefore the tetrahedron, for six-coordination the octahedron, for eight-coordination the square anti-prism and for nine-coordination the tricapped trigonal prism in which these metals ions used in theses display in solution as shown in Figure 4. The porous nature of Bamboo carbon make it easy for these competitive adsorption and the structure of these metal ions in solution makes bonding of these metals to the pores of bamboo carbon easier.

The work of Chen et al., (2010) while studying the adsorption of aqueous Cd²⁺, Pb²⁺, Cu²⁺ ions by nano-hydroxyapatite also similarly reported that the sorption affinity of nano-HAP for Pb(II) is always higher than that for Cu(II) and for Cd(II); the sorption maxima for the Cd, Pb and Cu follow the order Pb²⁺ > Cu²⁺ > Cd²⁺, which they reported could be inversely proportional to the hydrated ionic radii as Pb²⁺ (4.01 Å) > Cu²⁺ (4.19 Å) > Cd²⁺ (4.26 Å).

The amount of activated carbon adsorbed also increased with time until equilibrium was attained when higher metallic ion concentration of 500 mg/L of each metals salts in solution was used for adsorption and also more surface sites were covered as shown in Fig 6. It was observed that heavy metal ions are being adsorbed according to this order Pb>Cd>Cu>Zn>Ni>Cr. According to this order, chromium (Cr) was the least adsorbed and Pb was the most adsorbed, because the heavy metal whose complex is stable will be present in the complex at higher levels and this will cause the complex to be adsorbed more (Uzun & Guzel 2000). The capacities of the adsorbent get exhausted due to non-availability of active surface sites. It was also observed from Fig 6, that the amount of metal ions adsorbed, rapidly reached equilibrium from 120min before it became stable. Using higher concentration of adsorbate, (500 mg/L) there exist closeness in the amount of Copper and Cadmium adsorbed as well as the amount of Chromium and Nickel adsorbed. This difference can be attributed to the stability of these metallic complexes at higher concentration as compared with what happened at lower concentration in Fig. 4.

Fig. 5. Basic models for tetrahedron, octahedron, square antiprism, and tricapped trigonal prism.

Fig. 6 shows the amount of metal ions adsorbed in mg/g of carbon at different adsorption times for the different metal ions in aqueous solution (500 mg/L of each metal salt in aqueous solution).
4. CONCLUSION

Multiple batch adsorption of different heavy metal ions in aqueous solution using activated carbon from Nigerian Bamboo has been investigated. The results obtained from equilibrium study on batch adsorption of these heavy metal ions showed that Bamboo activated carbon can effectively be adopted in multiple adsorption of these heavy metal ions when present in waste water. An increase in contact time resulted in increase in the quantity of metal ions adsorbed till equilibrium was reached. It can also be seen that heavy metal ions are adsorbed in the following affinity order of adsorption Pb > Cd > Cu > Zn > Ni > Cr. Lead ions was the most adsorbed and Nickel ions the least adsorbed in the same aqueous solution. The order of adsorption is related to the maximum adsorption of lead, cadmium, copper on bamboo was found to be in the order of ionic radius of the heavy metals used. The high multiple adsorption intensity of activated carbon from Bamboo and its high affinity for metal ions of Nickel, Copper, Zinc, Lead, Cadmum, and Chromium can help resolve many adsorption challenges in the industry and in water purification processes. This research work on multiple adsorption of different heavy metal ions in an aqueous solution using activated carbon from Nigerian Bamboo has also contributed to the search for less expensive and easily available material for adsorption and separation process.

REFERENCES


