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# Adsorption Efficiency And Equilibrium Study of *Melaleucaleucadendron*Husk in The Removal of $Cu^{2+}$ And $Cd^{2+}$ Ions From Aqueous Solution

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***Abstract:****The possible utilization of Melaleucaleucadendron Husk based activated carbon as an adsorbent for the removal of methylene blue dye from aqueous solutions has been investigated. The adsorption of Cu (II) and Cd (II) ions from aqueous solution by the prepared activated carbon was studied at varying metal ion concentrations, adsorbent dose, contact time, temperature and pH. Batch adsorption studies were used. It was found that the capacity of adsorption depends on pH value. The highest percentage of metal removal was achieved with adsorbent dosage of 0.6 g, an initial concentration of 20 mg/l metal ion, particle size of 1.0 mm, pH of 6.0, contact time of 70 minutes and temperature of 313K. The removal percentage was found to be higher for $Cd^{2+}$ when compared with $Cu^{2+}$. The three most common adsorption equations, Temkin, Freundlich and Langmuir adsorption isotherms were used in the study to verify the adsorption performance. From interpretation of the equations, the Freundlich adsorption isotherm was found to fit the experimental data better than the other two. This suggests the formation of monolayer of Cu (II) and Cd (II) ions onto the outer surface of the adsorbents. Melaleucaleucadendron husk can be considered as potential adsorbent for the removal of Cu (II) and Cd (II) ions from aqueoussolutions.*

***Keywords:*** *Activated carbon, Heavy metal, Adsorption, Adsorption isotherm; Melaleucaleucadendron.*

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## I. INTRODUCTION

The problems of the ecosystem are increasing with developing technology. Heavymetal pollution is one of the main problems. This pollution by heavy metals is mainly caused by industrial and agricultural processes. Removal of heavy metals from wastewater is usually achieved by physical and chemical processes which include precipitation, coagulation, reduction, membrane processes, ion exchange and adsorption [1]. Activated carbon (AC) is widely used as an adsorbent for the removal of these heavy metals due to its high adsorption capacity. This capacity is related to the pore structure and chemical nature of the carbon surface in connection with preparation conditions [2].The effects of heavy metals in water and wastewater range from beneficial to toxic, depending on their concentration. Since heavy metal ions are not biodegradable in nature, effective removal of heavy metal ions from aqueous solutions and waste effluents through various technologies (physical or chemical) is important in the protection of environment and public health.Various chemical and physical methods have been used to remove metal ions from solutions in the past few decades. These methods include chemical

precipitation, solvent extraction, ion exchange, evaporation, reverse osmosis, electrolysis and adsorption. Among these methods, chemical precipitation, solvent extraction, ion exchange and adsorption are more commonly used [3]. Adsorption has been considered as, possibly, the most cost-effective method for heavy metal ion removal, especially at medium to low concentrations, because the process is simple and chemical consumption or waste generation is not a significant issue [4]. Gimba researched on the preparation and adsorption of activated carbon from coconut shell [5]. He reported that coconut shell carbon can be used for both laboratory and industrial purpose, depending on their method of preparation. Turoti*et al.* studied the effect of differentactivation methods on the adsorption characteristics of AC from *Khayasenegalensis*and *Delonixregia*pods [6]. They discovered that the order of effectiveness of the methods follows the sequence; two-step > microwave > impregnation > one step. Others include research on almond shell by Aygun*et al.* [7], peach stone by Tsai *et al.* [8], peanut hulls by Girgis*et al.* [9] and nut shells by Yang and Lua[10].*Melaleucaleucadendron* also known as weeping paper bark or Cajuput tree and is widely spread in tropical West Africa and extending eastward to Uganda, Kenya and Tanzania. It is also grown throughout the world as ornamental and as sources of wood [11]. It has a long-leaved paper bark or white paper bark flowering which can occur at any time of the year and is followed by fruits which are woody capsules, 3.9-4.9 mm (0.150.19 m) long in loose clusters along stems. *Melaleucaleucadendron* Husk is a common waste in Nigeria and other countries. The aim of this work was to assess the ability of *Melaleucaleucadendron* Husk to adsorb Cu (II) and Cd (II) ions from aqueous solutions. This aim was achieved by determining some physicochemical properties of the adsorbent and examining the effect of the solution pH, temperature, contact time, particle size and adsorbent dosage on the removal of Cu (II) and Cd (II) ions.

## II. MATERIALS AND METHODS

### 2.1 Sample Collection andTreatment

The adsorbents were prepared as described by [14]. Husks from MLH collected after discarding the fruit pulps, were sun dried, crushed and grinded in a ball mill individually. The grinded samples were sieved to obtain the particles of uniform size, 1.0 and 3.0 mm respectively. The ratio of acid to precursor was 2:1; i.e. 200 ml of acid w/v for every 100g of sample. The precursors obtained were washed to remove surface bounded impurities and mud then dried. The adsorbents prepared were denoted MLH-PA.After cooling, the carbonized sample was washed using 10% HCl to remove surface ash, followed by hot water wash and rinsing with distilled water to remove residual acid [14]. The solids were sun dried, then, dried in the oven at 105$^{o}$C for one hour.

Figures 1,2,3,4 and5 represent the tree and fruits from which the adsorbent was produced, the ground precursors and the prepared activated carbons.

### Characterization of the adsorbents

### Proximate Analysis

### Moisture content

The moisture content was found by oven-drying test method [15]. A sample of carbon was put into a dry, closed capsule (of known weight) and weighed accurately. The capsule is opened and placed with the lid in a preheated oven (145 – 155$^{o}$C). The sample was dried to constant weight then removed from the oven and with the capsule closed, cooled to room temperature. The closed capsule was weighed again accurately. The percentage difference of weight is expressed as the moisture content of the sample.

### Percentage volatile matter

The percentage of volatile matter of the AC samples was determined by the standard method [16]. Approximately 1.0 g of the sample was taken in crucible withcover (of known weight). The covered crucible was placed in muffle furnace regulated at 950$^{o}$Cfor 7 min. Then the covered crucible was cooled to room temperature in a desiccator and weighed. The percentage weight loss was regarded as the percentage of volatile matter.

### Ash content

To determine the ash content, dried sample of activated carbon was weighed to the nearest 0.1mg and taken into the crucible (of known weight). The crucible was placed in the muffle furnace at 650$^{o}$C and ashing was considered to be completed when constant weight was achieved. The crucible was cooled to room temperature in a desiccator and the percentage weight of the sample remained was considered as the ash content (ASTM D2866 – 94).

### Fixed carbon

Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter subtracted from 100.

*Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)* (2.1)

**Ultimate Analysis**

The ultimate analysis or elemental analysis was carried out by using CHNS analyzer (ElementarVario EL CUBE). The percentage of oxygen was calculated by the difference asfollows.

*Oxygen (%) = 100 – (C, % + H, % + N, % + S, %)* (2.2)

**Activated Carbon Yield**

The yield of activated carbon (AC) was calculated on a chemical-free basis and can be regarded as an indicator of the process efficiency for the chemical activation process. The yield of AC was calculated as the percentage weight of the resultant activated carbon divided by weight of dried precursor.

Yield % = weight of AC after carbonization/weight of raw material x 100 (2.3)

**Bulk Density**

The bulk density was estimated by placing the product into a graduated cylinder and compacted by tapping on the bench top until an expected volume ($cm^3$) was occupied by mass (g). The cylinder was tapped on the bench top until the volume of the sample stop decreasing. The mass and volume were recorded and density calculated as equation below [17]

$$\rho = \frac{mass}{volumeoccupied} \quad (2.4)$$

**pH measurement**

The 1% solution of the sample was made using deionized water. The pH of the supernatant was obtained after 1 h using a pre-calibrated pH meter (Oaklon pH meter, Model 1100).

**Determination of porosity based on swellings procedure**

The 0.5 g sorbent was dispersed in 20 mL water ($V_1$) in a graduated tube with the aid of a shaker. This was further centrifuged for 10 min at 2000 rpm using centrifuge (Baird and Tatlock Auto Bench). The resulting volume was read at $V_2$ and recorded. The equation 5 was used to calculate the porosity [17]:

$$\text{Porosity} = \frac{V_1}{V_2} \quad (2.5)$$

**Figure 1:** The fruits **Figure 2:** The tree

**Figure 3**: The ground precursor (1.0mm)**Figure 4**: The ground precursor (2.0 mm)

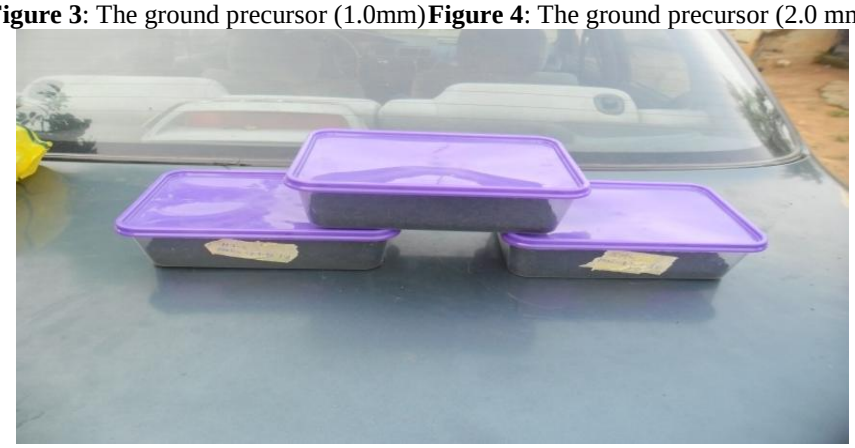

**Figure 5:** The prepared activated carbon (MLH-PA)

PA stands for Phosphoric acid

**Determination of iodine adsorption number of MLH**

The method used for the determination of iodine value was as that used by Itodo [18]. The iodine adsorption number (IAN) was calculated from the relationship as equation 6:

$$\text{IAN} = \frac{Ms\ (Vb - Vs)}{2Ma} \qquad (2.6)$$

Where $M_s$ is the molarity of thiosulphate solution (mol/dm$^3$), Vs is the volume of thio-sulphate (cm$^3$) used for titration of the AC aliquot, $V_b$ is the volume of thio-sulphate (cm$^3$) used for blank titration and Ma is the mass of AC (g).

**Preparation of Solutions**

The stock solutions of Cu (II) and Cd (II) ion were prepared by dissolving Cu $(NO_3)_2$ and Cd $(NO_3)_2$ in distilled water. The resulting solutions were diluted to obtained serial concentrations of Cu (II) and Cd (II) ion solutions. Batch adsorption experiments were conducted using MLH-PA as adsorbent in 120 mL polythene bottle or 300 mL reagent bottles containing 50 mL of various concentrations of Cu (II) and Cd (II) solutions. The bottles were agitated at 200 rpm in a thermostatic shaking incubator to reach the equilibrium. The effect of pH on the adsorption of the studied metal ions by MLH-PA was studied in the pH range 2.0 - 10.0 at 303 K. The solution pH was adjusted to the desired value with dilute HCl or NaOH solution using a pH meter (Oaklon pH meter, Model 1100). The effect of temperature on adsorption capacity of MLH-PA was studied at 303, 313, 323 and 333 K with the adsorbent dosage of 0.6 g/L at pH 6. The effect of dosage on the adsorption capacity of MLH-PA was determined at different dosages in the range 0.2 - 1.0 g/L of the studied metal ions at initial concentration of 20 mg/L. The effect of contact time on the adsorption capacity of MLH-PA was studied in the range 30 - 130 minutes at an initial concentration of 20 mg/L. Adsorption isotherms were studied at various initial concentrations of the studied metal ions in the range of 20 – 120 mg/L at varying temperatures of 303K, 313K and 323K. In each set of the experiment, the concentrations of Cu (II) and Cd (I) ions were determined using Perkin Elmer atomic absorption spectrophotometer. From the measured concentration of Cu (II) and Cd (II) ions, amount of the metal adsorbed ($q_e$) and the percentage metal ion removal (% Rem) was calculated using equations 2.7 and 2.8, respectively [19].

$$q_e = \frac{V\,(C_o - C_e)}{100\,M} \quad (2.7)$$

$$\% \text{ Rem} = \frac{C_o - C_e}{C_o} x\ 100 \quad (2.8)$$

where $q_e$ is the amount of adsorbate ion adsorbed in milligram per gram of the adsorbent, $C_o$ is the initial concentration of the metal ion before the adsorption process, $C_o$ is the equilibrium concentration of the metal ion in the filtrate after adsorption process, M is the mass in gram of the adsorbent and V is the volume of the solution in mL.

## III. RESULTS AND DISCUSSION

### 3.1 Physicochemical Analysis of MLH

The results obtained from the physicochemical parameters of the MLH are presented in Table 1. The percent dry matter and moisture of MLH are 89.703% and 5.82%, respectively. The percent moisture was lower than 6.48% reported by Erhan*et al.* [20] for cornelian cherry and lower than 5.75% reported by Shakirullah*et al.* [21] for sawdust. This high value may be as a result of its hydrophilic nature.The pH of MLH was found to be 5.74. This value falls within the acceptable pH conditions for adsorption [22]. Bulk density determines to a large extent the length of the filtration cycle of activated carbon [23]. The bulk density for MLH was found to be 0.591 g/cm$^3$. This value according to Erhan*et al.* [20] suggests that MLH is a good adsorbent in terms of volume activity. The ash content and porosity value of the sample were found to be within the range reported by other researchers [24]. This is favorable because it is relatively low. The lower the ash content (2.90) of MLH suggests that it is a better material for adsorption since the ash serves as interferences during the adsorption process [24].

**Table 1:** Physicochemical parameters of *Melaleucaleucadendron* husk

| Parameters | Melaleucaleucadendron husk |
|---|---|
| pH of 1% solution | 5.742 |
| Bulk density (g/cm$^3$) | 0.591 |
| Moisture content (%) | 5.82 |
| Dry matter (%) | 89.703 |
| Volatile matter (%) | 91.24 |
| Ash content (%) | 2.90 |
| Porosity | 0.942 |
| Iodine adsorption number (mM/g) | 0.1684 |

**Table 2:**Ultimate Analysis of *Melaleucaleucadendron* husk

| Parameters | *Melaleucaleucadendron* husk |
|---|---|
| C | 81.75 |
| H | 2.70 |
| N | 1.75 |
| S | 5.34 |
| O | 8.46 |

The iodine adsorption number (IAN) measures the adsorption of iodine from an aqueous solution. It is a measure of microspores and it is used as an indication of the total surface area. Adsorbents with high iodine number perform better in removing small sized contaminants. It is the most fundamental parameter used to characterize the performance of activated carbon. High value indicates high degree of activation [17]. From the result presented in Table 1 above, the IAN for MLH estimated in mM iodine per gram of adsorbent is fairly high (0.1684), as compared to that reported by Itodo [18] for Shea nut shells (0.1338 - 0.1505) and groundnut shells (0.1115 - 0.1394). It thus implies that MLH presents high degree of activation and high affinity for small sized contaminants.

### 3.2 Batch Studies

#### 3.2.1 Effect of particle size

Table 3.0 shows the effect of particle size on the adsorption of Cu (II) and Cd (II) by MLH. It is seen that the removal of heavy metals increases as the particle size diameter decreases. According to Kumar *et al.* [25], decrease in particle size increases the percentage removal due to increase in surface area as well as micropore volume. Smaller particle size means more interior surface and micropore volume and hence more will be the area of active sites for adsorption. Also for larger particles the diffusion resistance to mass transfer is higher and

most of the internal surfaces of the particle may not be utilized for adsorption and consequently the amount of the studied metal ions adsorbed is small [26]. Therefore the optimum particle size in this study is 1.0 mm.

**Table 3.0:** Amount of metal ion adsorbed and removal efficiency at equilibrium by various sizes of MLH

| Size (mm) | Copper | | Cadmium | |
|---|---|---|---|---|
| | $q_e$ (mg/g) | % Rem | $q_e$ (mg/g) | % Rem |
| **1** | 0.5213 | 68.40 | 0.5285 | 69.49 |
| **3** | 0.5048 | 65.00 | 0.5128 | 66.03 |

**3.2.2Effect of initial metal ion concentration**

The initial concentration of metal ions in the solution is an important parameter as the metal concentration changes over a broad range in industrial effluents. Figure 3.1, 3.2 and 3.3 depicts the changes in adsorption trends of MLH-PA with variation in initial concentration of adsorbate in the solution and at definite experimental conditions: pH of 6.0, particle size of 1.0, adsorbent dose of 0.6 g (in 30 mL solution), shaking speed (200 rpm), contact time (70 min) and at varying temperature of 303K, 313K and 323K. The initial metal concentrations studied were (20, 40, 60, 80, 100, 120 mg $L^{-1}$). As shown in Figure 3.1, 3.2 and 3.3, the percentage of adsorbate ions adsorption decreased with increasing initial concentration from 20–120 mg/L. The reason for the decrease in adsorption efficiency can due to the relatively smaller numbers of active sites available on MLH-PA. The decrease in percentage removal can also be explained by the fact that as the concentration of the adsorbate increases so does the metal loading on the adsorbent [27]. For instance, a concentration of 100mg/L will have higher surface loading compared to concentration of 20 or 40mg/L. While on the other hand the number of adsorbing sites available for the adsorption is constant for all concentration. So, when the concentration is higher, more ions will be competing for the same adsorption sites and will go through without being adsorbed [27]. However, at higher concentrations, active sorption sites are not sufficiently available for the adsorbates to occupy. Hence the adsorbates were not completely adsorbed from solutions due to the saturation of binding sites. In addition, the adsorbed adsorbate ion electrostatically repels the incoming sorbet ions resulting in decrease of the adsorption percentage. These results are consistent with other reports [28]. Hence the optimum concentration is 20.0 mg/L. The rate of adsorption on the adsorbents at different temperatures is illustrated in Figures 3.1, 3.2 and 3.3. The figures represents high rate of adsorption at 313K, however low rate of the adsorbates adsorption were observed at 303K within studied range of time. Therefore the optimum temperature is 303K. At higher temperatures the rate of diffusion of solute within the pores of the adsorbents increases since diffusion is an endothermic process. Thus, the percentage adsorption of the adsorbates increases as the rate of diffusion of adsorbate ions in the external mass transport process increases with temperature [28]. Moreover, at low temperatures the kinetic energy of adsorbates species is low and hence contact between the metal ions and the active sites of MLH-PA is insufficient, resulting in reduced adsorption efficiency compared to higher temperature. Increased adsorption with temperature may also be due to the increase in number of adsorption sites generated as a result of breaking of some internal bonds near edge of active surface sites of adsorbent [29].

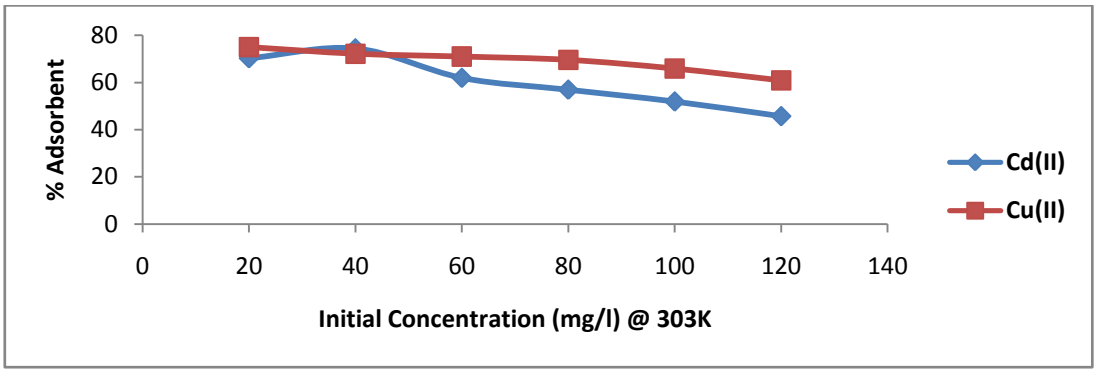


Figure 3.1: Effect of initial concentration 20 – 120 mg/L on the adsorbates removed by MLH-PA ([Cd (II) and Cu (II)]: pH of 6 for Cd (II) and Cu (II); shaking speed: 200 rpm, contact time: 70 minutes, at 303K, n = 3 for each contact time for all adsorbents).

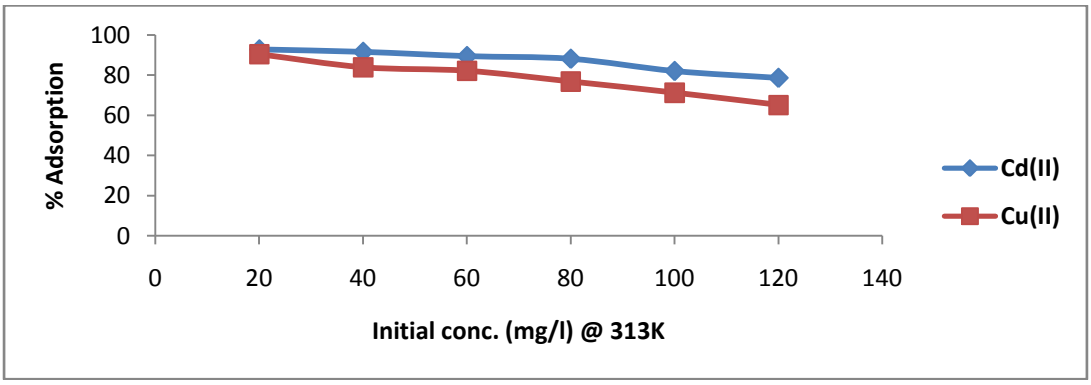


Figure 3.2: Effect of initial concentration 20 – 120 mg/L on the adsorbates removed by MLH-PA ([Cd (II) and Cu (II)]: pH of 6 for Cd (II) and Cu (II); shaking speed: 200 rpm, contact time: 70 minutes, at 313K, n = 3 for each contact time for all adsorbents).

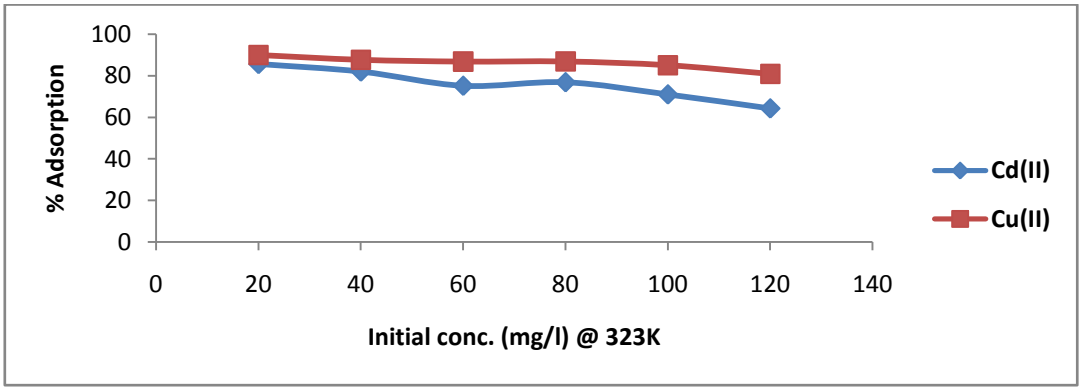


Figure 3.3: Effect of initial concentration 20 – 120 mg/L on the adsorbates removed by MLH-PA (Cd (II) and Cu (II): pH of 6 for Cd (II) and Cu (II); shaking speed: 200 rpm, contact time: 70 minutes, at 323K, n = 3 for each contact time for all adsorbents).

**3.2.3. The effect of initial solution pH**

The pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So the pH of the aqueous solution is an important controlling parameter in the heavy metal adsorption process [30]. The effect of pH on the adsorption of Cd (II) and Cu (II) by MLH-PA is shown in Figure 3.4. The effect of solution pH on the adsorption of metal ions onto the adsorbents was evaluated in the pH range of 2 to 10. The

binding of Cu (II) and Cd (II) with surface functional groups strongly depended on the pH of solution. The removal efficiency of Cu (II) and Cd (II) increased with pH of the solution because Cu (II) and Cd (II) forms complex with some functional groups in the adsorbent. The removal of metal cations at any pH was much greater than that by hydroxide precipitations. Adsorption of metal cations on adsorbent depends upon the nature of adsorbent surface and the distribution of metal species which distribution also depends on the pH of the solution [30]. The removal efficiency of Copper and Cadmium decreased with the decrease of pH, because protons compete with metal ion for the adsorption sites on the adsorbent surface as well as the ion existing decrease of negative charge by association of the functional group with proton. The increase in metal ion removal as pH increase can be explained on the basis of the decrease in $H^+$ on the surface, which results in less repulsion with adsorbing metal ions [31]. In this study, it was confirmed that optimum pH for the adsorption of Cu (II) and Cd (II) is 6. Only an insignificant increase was observed after this pH.

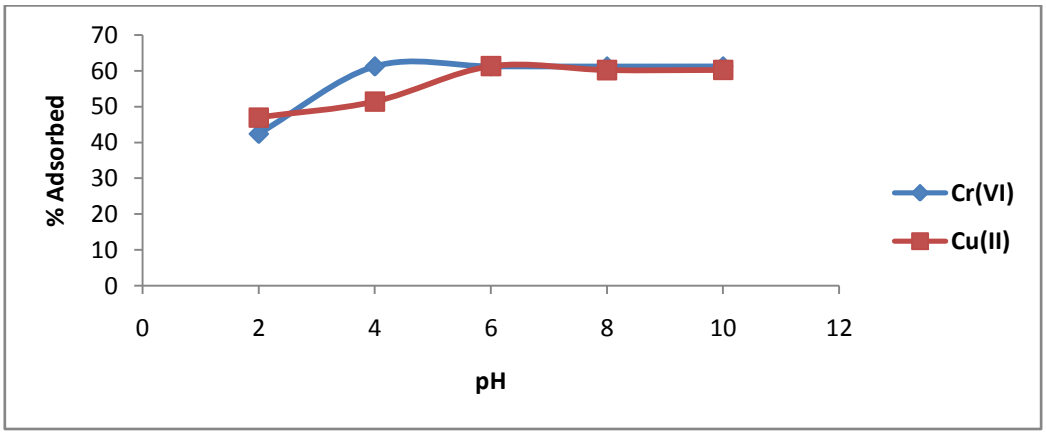


Figure 3.4: Effect of pH 2-10 on the adsorbates removed by MLH-PA ([Cd (II) and Cu (II)]: 20 mg/l, pH of 2-10, shaking speed: 200rpm, contact time: 70 minutes, and temperature: 25°C, n = 3 for each contact time for all adsorbents).

### 3.2.4: Effect of adsorbent dosage

Adsorbent dose variation experiment is one of the significant parts of the study that determines the capacity of adsorbents for a given initial concentration of the adsorbates [Cd (II) and Cu (II)] at the operating circumstances. Thus the experiments were carried out by varying adsorbent doses only in the range 0.1–1.0 g at 25 °C. The effect of adsorbent dose on the adsorption of adsorbates by the adsorbents is shown in Figure 3.6. Optimum adsorbate efficiency removal was achieved at an adsorbate dose of 0.6 g for MLH-PA

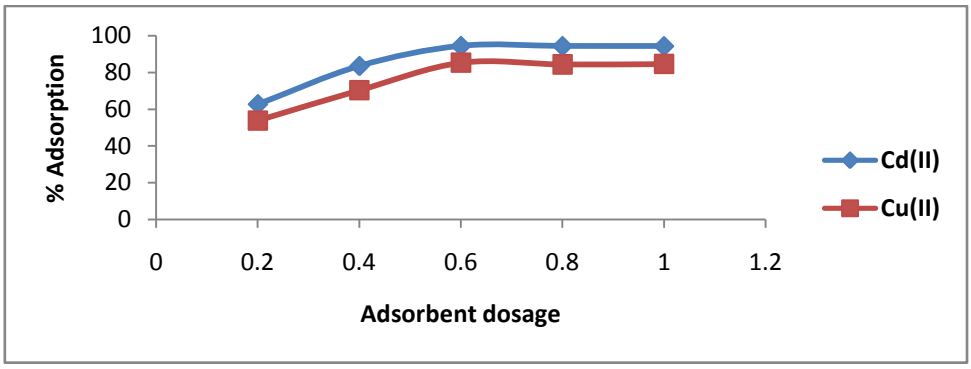


Figure 3.5: Effect of adsorbent 0.2 – 1.0 g on the adsorbates removed by MLH-PA ([Cd (II) and Cu (II)]: 20 mg/l, pH of 6 for Cd (II) and Cu (II); shaking speed: 200 rpm, contact time: 70 minutes, and temperature: 25°C, n = 3 for each contact time for all adsorbents).

### 3.2.5: Effect of contact time

The figure 3.6 below shows that the percentage uptake increases with time and after some time, it reaches a

constant value where no more metal ion can be removed from the solution [30]. At this point, the amount of metal ions being absorbed by the adsorbent was in a state of dynamic equilibrium with the amount of metal ions desorbed from the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time. The amount of metal ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under these particular conditions. The result showed that the adsorption of metal ion increases with time up to 70 min and then it becomes almost constant at the end of the experiment.

In general, the initial rate of adsorption was fast, and then a slower adsorption was follow as the available adsorption sites were slowly decreased. These is due to the fact that a large number of unoccupied surface sites are available for adsorption during the initial stage and after ascend of time the remaining unoccupied surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [32]. Then from the results obtained the optimum contact time for adsorption onto adsorbents was fixed to be 70 minutes since the adsorption removal became constant after this contact time.

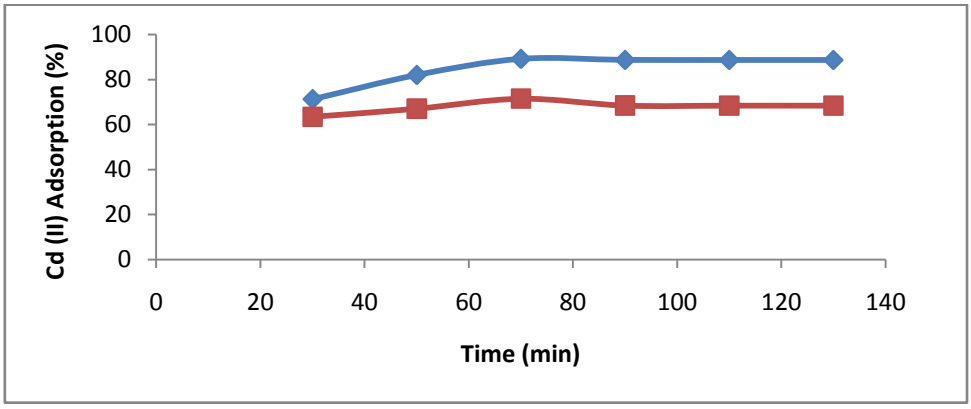


Figure 3.6: Effect of contact time 30-130 minutes on the adsorbates removed by MLH-PA ([Cd (II) and Cu (II)]: 20 mg/l, pH of 6 for Cd (II), Cu (II), shaking speed: 200rpm, adsorbent dose 0.6 g/100mL, and temperature: 25 °C, n = 3 for each contact time for all adsorbents).

### 3.2.6.Effects of temperature

Temperature is a highly significant parameter in the adsorption processes. For adsorption of $Cu^{2+}$ and $Cd^{2+}$ ions onto MLH, adsorption experiments were run to study the effect of temperature variation at 303, 313, 323 and 333 K at optimum pH value of 6 and adsorbent dose level of 0.6 g/L. The equilibrium contact time for adsorption was maintained at 70 min. The results presented in Table 3.3 shows that the percentage of adsorption increased along with an increase of temperature and then later decreased with no observable increase. This could be due to increase in average kinetic energy of the metal ions in solutions containing the adsorbent which increases the number of metal ions colliding with the adsorbent surface by increasing the rate at which the metal ions hit the binding sites at the surface of the adsorbent thus increasing the adsorption capacities [33].

**Table 3.3:** Amount of metal ion adsorbed and removal efficiency at equilibrium by MLH-PA at various temperatures

| Temperature | Copper | | Cadmium | |
|---|---|---|---|---|
| | $q_e$ (mg/g) | %Rem | $q_e$ (mg/g) | %Rem |
| **303** | 0.4631 | 70.45 | 0.4612 | 70.28 |
| **313** | 0.4671 | 70.47 | 0.4700 | 70.33 |
| **323** | 0.4668 | 70.41 | 0.4615 | 70.27 |

### 3.3. Isothermal studies

`The adsorption isotherms reveal the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. To quantify the adsorption capacity of MLH-PA for the removal of $Cu^{2+}$ and $Cd^{2+}$ ions from aqueous solution, the Langmuir, Freundlich and Temkin isotherm models were used.

#### 3.3.1. Langmuir adsorption isotherm

The Langmuir isotherm is applicable to homogeneous sorption where the sorption of each sorbate molecule on to the surface has equal sorption activation energy and is represented as follows [34]

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \qquad 3.1$$

Where $q_e$ is the solid phase sorbate concentration at equilibrium, $K_L$ and $a_L$ are the Langmuir isotherm constants. The linear form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad 3.2$$

The adsorption data were analyzed according to the linear form of equation (equation 4.9). The plots of $C_e/q_e$versus $C_e$ are linear which indicate that the adsorption data fitted reasonably to the Langmuir isotherm shown in Figure 3.6 (a) and (b). The constants were evaluated from the slope $a_L/K_L$ and intercept $1/K_L$, where $K_L/a_L$ gives the theoretical monolayer saturation capacity $Q_o$. The Langmuir constants obtained for all the three adsorbents are summarized in Table 3.4. The negative value of $a_L$ obtained for MLH-PA indicates the inefficiency of Langmuir model to explain

$$R_L = \frac{1}{1 + a_L C_i} \qquad 3.3$$

Where, $C_i$ and $a_L$ are the initial concentration and constant related to the affinity of binding sites with the metal ions, respectively. The value of $R_L$, a positive number ($0 < R_L < 1$), signifies the feasibility of the adsorption process for MLH-PA.

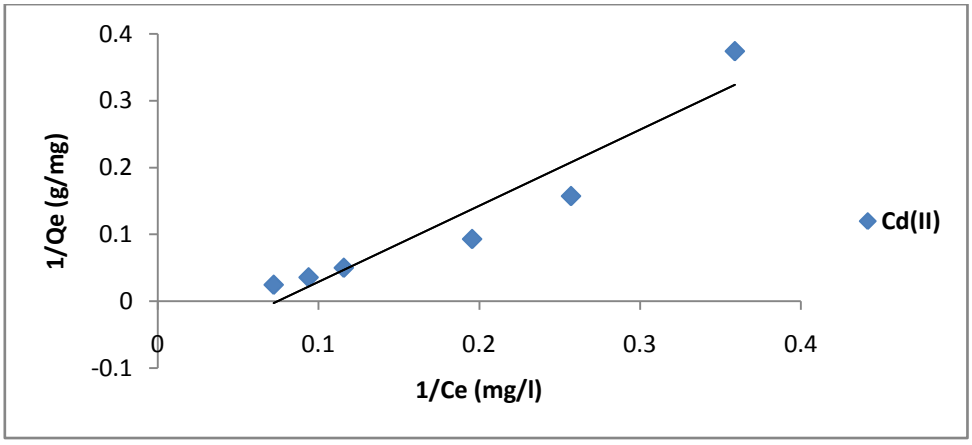


**Figure 3.6 (a)**: Langmuir adsorption isotherm for $Cu^{2+}$ adsorption by MLH-PA

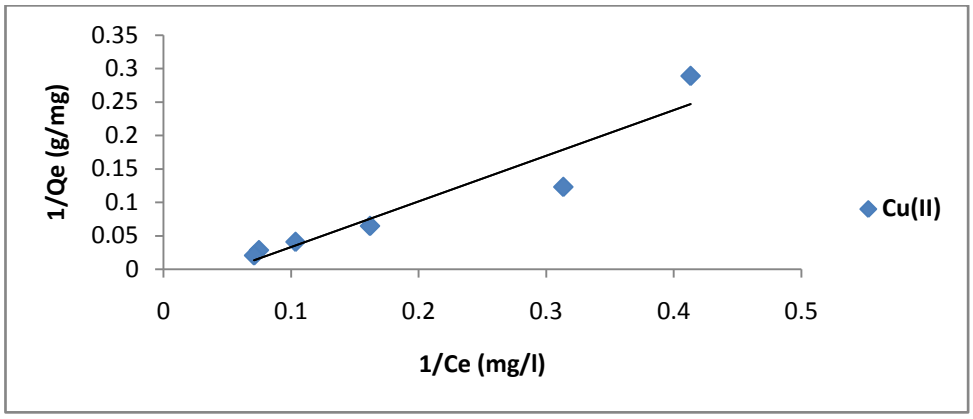


**Figure 3.6 (b)**: Langmuir adsorption isotherm for $Cd^{2+}$ adsorption by MLH-PA

### 3.3.2 Freundlich Isotherm model

The most important multisite or multilayer adsorption isotherm for heterogeneous surfaces is the Freundlich isotherm which is characterized by the heterogeneity factor 1/ n, and is represented by the equation:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad 3.4$$

Where, $q_e$ is the solid phase concentration in equilibrium, $C_e$ is the liquid phase sorbent concentration at equilibrium; $K_F$ is the Freundlich constant and 1/ n is the heterogeneity factor.

The magnitude of n gives an indication on the favorability of adsorption. It is generally stated that the values of n in the range 2 – 10 represent good, 1 – 2 moderately good, and less than 1 poor adsorption characteristics [35]. The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. The linear form of Freundlich equation is:

$$\text{In } q_e = \text{In } K_f + \frac{1}{n} In\ C_e \qquad 3.5$$

Where, the intercept ln $K_F$ is a measure of adsorption capacity, and the slope 1/ n is the adsorption intensity. The values of $K_F$ and n were calculated from the intercept and slope of the plots $\ln q_e$ against $\ln C_e$ Figure 3.7 (a) and (b). The Freundlich isotherm showed a better fit to the adsorption data than Langmuir isotherm suggesting heterogeneous nature of MLH-PA

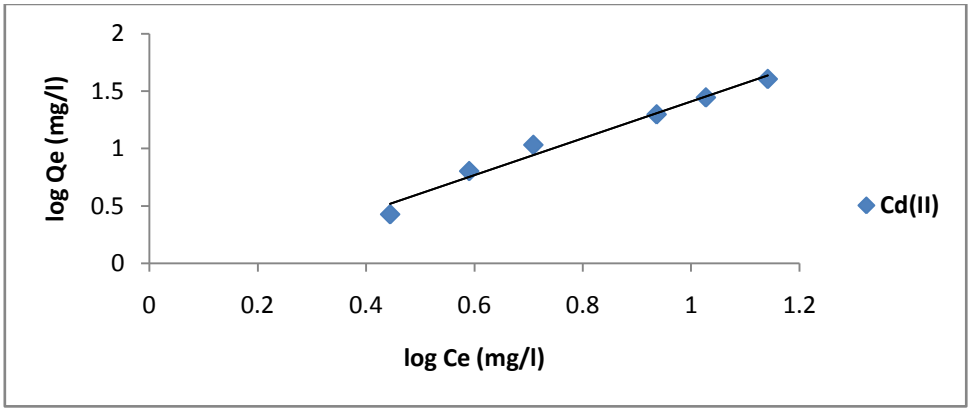


**Figure 3.7 (a):**Freundlich adsorption isotherm for $Cu^{2+}$ adsorption by MLH-PA

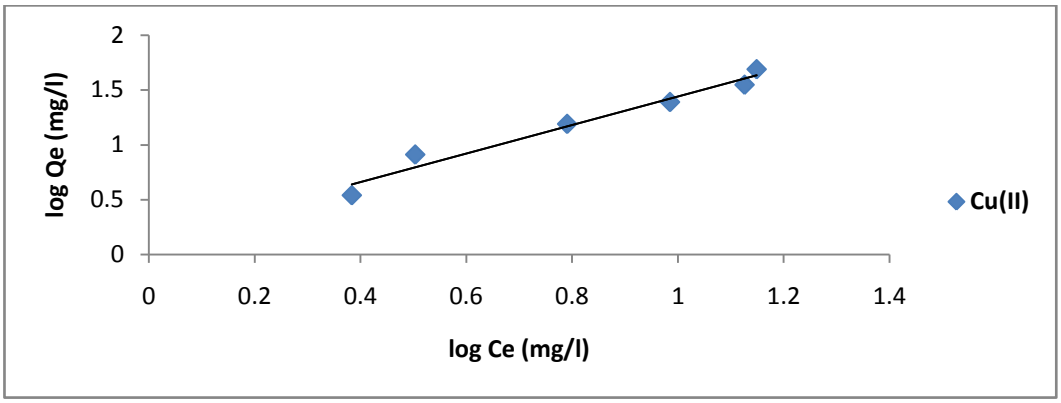


**Figure 3.7 (b):**Freundlich adsorption isotherm for $Cu^{2+}$ adsorption by MLH-PA

### 3.3.3 Temkin isotherm

Temkin isotherm model contains a parameter that explicitly accounts for the interaction of adsorbent and adsorbate species. It is based on the assumption that the heat of adsorption of all the molecules in the layer diminishes linearly with coverage which is attributed to adsorbate– adsorbate repulsions. It also assumes that adsorption is due to uniform distribution of binding energy. Contrary to Freundlich model, it assumes that fall in heat of adsorption is linear rather than logarithmic. The Temkin equation can be given as [36]

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad 3.6$$

Where $B_T = \frac{RT}{b}$, T (K) is the absolute temperature, R is the universal gas constant (8.314 J/K mol); $A_T$ (L/mg) is the equilibrium binding constant that corresponds to the maximum binding energy; $B_T$ is related to the heat of adsorption; and $q_e$and $C_e$ are the amount of adsorbate adsorbed per unit weight of adsorbent and equilibrium concentration of adsorbate remained in solution, respectively. The Temkin isotherm parameters were obtained by plotting $q_e$ versus $\ln C_e$ shown in Figure 3.8 (a) and (b) The positive values (Table 3.4) of adsorption energy ($B_T$) obtained indicate that the process is exothermic, which is contrary to the obtained results. The low $R^2$ values obtained suggest that the adsorption data does not follow the Temkin isotherm.

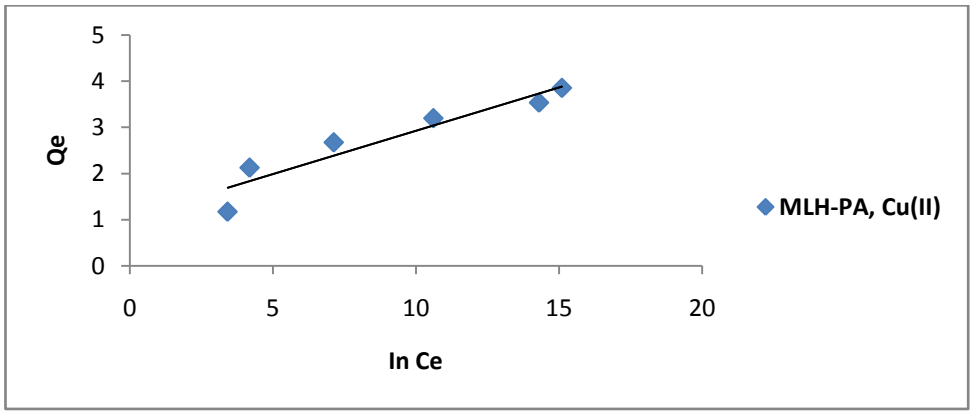


**Figure 3.8 (a):**Temkin adsorption isotherm for $Cu^{2+}$ adsorption by MLH-PA

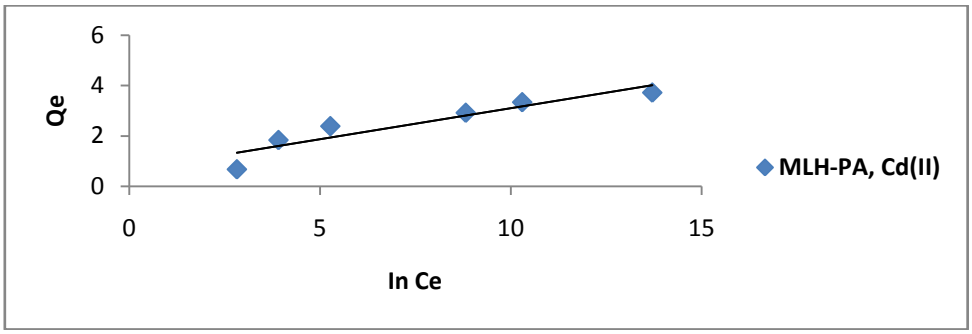


**Figure 3.9 (b):** Temkin adsorption isotherm for $Cd^{2+}$ adsorption by MLH-PA

**Table 3.4:** Constants for the adsorption of $Cd^{2+}$ and $Cu^{2+}$ on activated carbon prepared from MLH-PA

| **Isotherm Parameter** | **MLH-PA** | |
|---|---|---|
| **Langmuir** | Cd (II) | Cu (II) |
| $K_L$ (L/g) | 2.81 | 5.33 |
| $a_L$(L/mol) | 3.14 | 1.47 |
| $Q_o$ (mg/g) | 1.01 | 3.14 |
| $R_L$ | 0.01 | 0.16 |
| $R^2$ | 0.941 | 0.963 |
| **Freundlich** | | |
| $K_f$ [(mol/g)(mol/L)$^n$] | 4.19 | 3.87 |
| 1/n | 0.143 | 0.423 |
| $R^2$ | 0.991 | 0.971 |
| **Temkin** | | |
| $B_T$ | 2.14 | 0.64 |
| AT (L/mg) | 10.18 | 19.11 |
| $R^2$ | 0.898 | 0.867 |

The straight line plots of Langmuir and Freundlich adsorption isotherm models indicate that the adsorption of $Cu^{2+}$ and $Cd^{2+}$ on MLH-PA follows Langmuir and Freundlich isotherms. The higher value of correlation coefficient ($R^2$) for Freundlich in the adsorption of $Cu^{2+}$ ($R^2$= 0.991) and $Cd^{2+}$($R^2$ = 0.971) than for the other two isotherms indicates that the experimental adsorption data provided better fit in Freundlich isotherm model. This suggests the formation of monolayer of $Cu^{2+}$ and $Cd^{2+}$ ions onto the outer surface of the adsorbent. The positive values (Table 3.4) above of adsorption energy ($B_T$) obtained indicate that the process is exothermic, which is contrary to the obtained results. The low $R^2$ values obtained suggest that the adsorption data does not follow the Temkin isotherm.

## IV. CONCLUSIONS

From the present study, the following conclusions are drawn:

(1) Activated carbon prepared from MLH-PA was found to be a promising adsorbent for the removal of $Cu^{2+}$ and $Cd^{2+}$ ions from aqueous solutions.

(2) The sorption capacity of MLH-PA was strongly dependent on the adsorbent nature and dosage, initial metal ions concentration, temperature, and initial pH.

(3) The experimental data well fitted to the Freundlich equations with good correlation coefficients. This suggests the formation of monolayer of $Cu^{2+}$ and $Cd^{2+}$ ions onto the outer surface of the adsorbents

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