Adsorption of Copper (II) Ion by Leucaena Leucocephala Pods

Razak, N.H.A, Nur Amalia Zulkepli, Juferi Idris

Abstract: In this work, the efficiency of Leucaena leucocephala pods, an agricultural waste, to remove copper (Cu) ions in aqueous solution by adsorption. Batch mode experiments were carried out at 30 °C to study the influence of pH, contact time (t) and dosage on the adsorption of Cu by Leucaena leucocephala pods. The surface behaviour and the composition of the Leucaena leucocephala pods was characterized using pH of point of zero charge (pH_{PZC}), Fourier transform infrared spectroscopy (FTIR). It is shown that Leucaena leucocephala pods adsorbent can effectively remove Cu from aqueous solutions. The best sorption results were obtained at pH 8.0, 0.75 g dosage and within time 80 min. The FTIR studies indicated was existence of surface hydroxyl, carboxyl and carbonyl groups. Adsorption method was used to successfully execute post adsorption elution of the loaded metal.

Keywords : Adsorption, copper ions, Leucaena leucocephala pods

I. INTRODUCTION

Nowadays, the presence of the heavy metal in industrial and wastewater has been arise giving high toxicity of concentration that give impact to the public health. The concentration of heavy metal is the main thing that has been focused in the Malaysia is the due to the coastal resources, agriculture and economic activities and human population. Thus, it is an effective idea of removing the heavy metals from wastewater for a better future.

The increasingly usage of heavy metals over the years actually gave big impacts such as an enlarged of metallic constituents in the seas or oceans (aquoic environment). The main source of heavy metals usually comes from industrial activities. Other than industrial activity, ore mining, volcanic activity, forest fire, acid rain and also agriculture also donated high percentage in producing heavy metals in water content. Heavy metals is may result to the cancer and other health diseases due to the bio-accumulation of the body when exposed to the heavy metals through consumption. Amongst all the heavy metals, copper metal is one of the popular heavy metal that content high concentration in water resources that becoming water contaminants. In addition, copper metal also contribute to the heavy health diseases such as haemolysis, cirrhosis, anaemia, nephrotoxic and hepatotoxic effects and even can causing death. However, the efforts to overcome or prevent as far as possible the high content of heavy metals in surrounding are by carrying out the initiative methods for examples, chemical precipitation [1], electrolytic recovery [2], adsorption/ion exchange [3], and solvent extraction/liquid membrane separation [1]. Among all of these, adsorption is the most efficient way due to its high reliability, have simple design and sludge free operation. The most widely used absorbent so far is activated carbon which carbon which is very expensive. Therefore, there is a need to search of other adsorption potential that would provide low cost. One of the agricultural content that has received attention in the present study is the Leucaena leucocephala, which is able to the tune of tons per annum in Malaysia [4]. There is an estimated 15% of total waste generation consists of agriculture waste in Asia and Malaysia contribute 0.122 kg/cap/day consists of waste generation [5]. It is easily found, abundant, readily available at low cost and also environment friendly substance.

As the development of technologies increases more contaminating materials will be produced. For instance, the emission of heavy metals in ore processing and other industries have caused the public to be concerned. Eventually this will then lead to the development of restrictions, laws and even waste treatment technologies The build-up of industrial waste is dangerous and has becoming one of the problems of the world and society today therefore it is important to overcome this problem. There are many ways in handling this matter however in this paper the adsorption of toxic substance in the waste will be focused on. Hence, over the year’s researchers have been studying on the adsorption technique especially on methods that are effective in adsorption of the contaminant. This is because in general the adsorption technique consists of processes that uses high cost technologies therefore, to reduce the burden of the cost there is a need in improving the adsorption technique.

The objective of this paper is to evaluate the ability Leucaena leucocephala pods for removal of Cu (II) ions in aqueous solution. The effect of solution pH, adsorbent dosage, contact time on the removal of Cu (II) ions were studied.
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II. METHODOLOGY

A. Chemical reagents

Stock solutions of Cu(II) with concentration of 1000 ug/L were purchased from Inorganic Ventures. The hydrochloric acid (37%, ACROS Organics) and ethanol (37%, Fischer Scientific) were used for the modification of raw material.

B. Materials

The locally dried Leucaena leucocephala pods (LLP) were collected around Section 7, Shah Alam (Malaysia). The seeds were separated from the pods. Afterwards, they were grinded into small pieces and sieved at a mesh size of 400-μm using sieve shaker (Endecotts Octagon 2000 Digital), and then put into sealed plastic bag to be stored in a desiccator.

C. Methods

1) Preparation of Leucaena Leucocephala Bio-adsorbent

To dispose of dust other impurities, the bio-adsorbent will be washed with first tap water then use the deionized water. Then it was dried at 100°C until constant weight for 72 hours. After that, the LLP is keep in dehydrated state for the next experiment.

2) Chlorophyll removal of Leucaena Leucocephala pod

Ethanol was used for the extraction of chlorophyll from Leucaena Leucocephala pods. The parameters were obtained from [6]. The parameter was performed, at room (20 - 25°C) on a magnet stir plate with stir rate of 100 rpm. The residue obtained from ethanoic solution by filtered LLP and it will oven dried 24 hours at 105°C.

3) Chemically Modified of Leucaena Leucocephala pod

The modification of LLP were prepared according to [7]. 200 mL of distilled water in the 250 mL of beaker was boiled until it reached 100°C. The 100 g of dried LLP the added into the beaker. The mixture was stirred at 220 rpm and at 200°C for 10 minutes. The residue from solution was filtered after cooling and the residue was oven dried overnight to a constant weight at 105°C. Modification surfaces of adsorbent; hydrochloric acid (HCl) was used. Then, 50 g Leucaena Leucocephala pods was contacted with 500 ml of 0.1N HCl . After that, the mixture was stirred for 3 hours at 50 °C with a 300 rpm. The residue was filtered and rinsed with distilled water to pH 7. Then it was dried for 48 hours the next experiment.

4) Metal solutions

The solutions copper (II) ions were prepared by diluting a 50ppm stock metal ion solution. In the experiment, 250 mL volumetric flask with stopper cork along with 100 mL solution desired 50 ppm Cu (II). To produce a stock solution of 50 ppm, the flask was then filled with distilled water until reached the marked level [7].

5) Batch experiment for adsorption of Cu(II) ion

The adsorption of copper ions from aqueous solution was conducted in batch experiments at parameter variables such as pH of solution (2–12), time intervals (10 to 180 min), adsorbent dosages (0.5 g to 2.0 g). The pH values have been adjusted with 0.1 M NaOH and 0.1 M HCl. The pH values of Cu (II) solutions were measured by pH meter (Metttlor toledo).

The experiments were performed using orbital shaker at 250 rpm at 25 ± 1°C and capped 250 mL of Erlenmeyer flasks. The amount of metal adsorbed analysed by Inductive Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES). Then measure the adsorption capacity of Leucaena pods for Cu(II) using a mass balance equation as detailed by (Basu, Guha, & Ray, 2017)

\[ q = (C_i - C_f)/W \times V \]  

in this equation q is the amount of adsorbed uptake (mg/L), C_i initial metal ion concentrations and C_f final metal ion concentrations (mg/L), W; weight of adsorbent (g) and V; volume of solution (L).

6) Characterization of biosorbent

Fourier Transform Infrared Spectroscopy (FTIR) is to study the functional groups inside the sample of Leucaena Leucocephala pods within the range of 500 to 4000 cm⁻¹. Thermogravimetric Analysis (TGA) (Mettler Toledo TGA851/1600) is used to determine chemical composition inside the adsorbent by heating the biomass. As a function of temperature, the chemicals can be indicated by weight loss of the biomass during heating process. TGA is conducted by using nitrogen gas. The temperature range is from 0 to 1000°C and will be setting up and the heating rate used in TGA is setting up to 20°C/min.

III. RESULTS AND DISCUSSION

A. Characterization of the adsorbents

1) FTIR

By identifying the different types of functional groups existing on Leucaena Leucocephala pods was by studying the FTIR analysis of the sample. In order to know the surface binding mechanism, functional groups need to identify on the biomass [8]. The presence of carboxyl, hydroxyl, carboxyl, amide and amine, on the surface of the biomass have tendency for removal of Cu(II).

The FTIR spectra in Fig. 1 shows the raw, modified and after Cu (II) adsorption of Leucaena Leucocephala pods. The broad peak that assigned to hydrogen bonded OH groups and chemisorbed water is 3350–3446 cm⁻¹. This peak indicating the hydroxyl groups were formed on the surface of LLP.[9]. At 1736 cm⁻¹ appears C=O stretching vibrations of carboxylic groups (-COOH, -C=OCH3) which can be ascribed to esters or carboxylic acids [10]. This appeared a sharper peak at after adsorption, which indicates that carboxylic groups appear after adsorption.

While the peaks at 2918 cm⁻¹ and 2850 cm⁻¹ indicate C–H stretching vibrations disappear after modification indicating that indicate C–H was removed on surface [10]. FTIR spectra of modified Leucaena Leucocephala pods shows the shifting peak from 1019.07 cm⁻¹ to 1030.9 cm⁻¹, which shows an increasing in stretching of O-C-O.

Furthermore, the peaks detected 1604, 1515 and 1460 cm⁻¹ denoted aromatic ring vibration and deformation of C-H vibration in lignin [11]. This peak was not found in modified LLP. This result confirmed that the removal of lignin in the modified LLP.
The peak that appears after modified and Cu (II) adsorption at 1506.3 cm\(^{-1}\), 1423.6 cm\(^{-1}\) and 1365.6 cm\(^{-1}\) showing that some modifications in functional groups of LLP after modification with HCl, which is C=O (anhydride, carboxylic, ketone and lactone) at 1506.3 cm\(^{-1}\), O–H bending (lactonic, ether, phenol, etc. and C–O stretching at 1365.6 cm\(^{-1}\) and 1423.6 respectively[12].

Fig. 1. FTIR spectra raw Leucaena Leucocephala pods and after Cu (II) adsorption, A = raw Leucaena pods, B = modified Leucaena Leucocephala pods, C = after adsorption

B. TGA Analysis

TGA for the thermal behaviour of raw and modified Leucaena Leucocephala pods that had been plotted is presented in Fig. 2 and Fig. 3 respectively. The thermogravimetric (TGA) analysis was assessed to evaluate the thermal stability of the Leucaena Leucocephala pods for raw and modified pods studied in this research. The TGA graph shows in the weight loss in range temperature from 20°C to 50°C in sample which is about 5.4% and 6.7% for raw and modified Leucaena Leucocephala pods respectively due to evaporation of moisture content. Moisture content shows an increase in modified LLP. In modification with HCl, the swelling of the fibre takes place, therefore capillary will be absorption the moisture [13];[14]. The modified LLP became hydrophilic after the modification with HCl due to moisture loss from about 5.4% to 6.7% .

Biomass material was decomposed by heating in the range 200 to 400 °C contain glycosidic bond composition resulting in carbon dioxide, water, hydrocarbon derivatives and alkanes.. Hemicellulose, cellulose and lignin have different chemical structures, therefore it may decomposed at different temperatures. Acetyl group in hemicellulose begins to decompose at 220–300 °C [13]; [15]; [16].

Table I showed raw LLP started to degrade at 288°C (6.79% weight loss) because of hemicellulose decomposition and then continuous degradation until 326°C (39.97% weight loss). This is due to hemicellulose decomposes before cellulose and lignin. Acetyl groups in hemicellulose reduce thermal stability of hemicellulose [17][15]. This result is similar with other findings [18]; [19]; [20].

Fig. 2 Thermogravimetric analysis (TGA) analysis for raw Leucaena Leucocephala pods (LLP)

Fig. 3. Thermo gravimetric analysis (TGA) analysis for modified Leucaena Leucocephala pods (LLP)

T\(_{on}\) of modified LLP was higher than raw LLP since modified LLP removed lignin and hemicellulose. For the second peak at 367°C (mass loss 59.28%) corresponds to the thermal decomposition of the alpha cellulose and the cleavage of glucosidic linkages of cellulose [18], [19]. This results similar with other authors stated that cellulose decomposes at 310–400 °C [17],[13].

Furthermore, the T\(_{max}\) for modified LLP and raw LLP represent 326°C and 367°C. This difference may be due to removal of the protective waxes and lignin layers from the fiber. The modification with HCl remove other components then modified LLP had higher stability at high temperature [21].

Furthermore, above 550 °C there was almost no weight loss. Therefore, the temperature range over 600 °C was the curve depicts a straight line, which means a stable state. [22], [23].
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Table 1: Thermal properties of raw and modified Leucaena Leucocephala pods

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_{on} (°C)</th>
<th>Weight loss (%)</th>
<th>T_{max} (°C)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw modified Leucaena Leucocephala pods</td>
<td>288.16</td>
<td>5.4</td>
<td>326.3</td>
<td>39.97</td>
</tr>
<tr>
<td>Modified Leucaena Leucocephala pods</td>
<td>320.59</td>
<td>6.79</td>
<td>367</td>
<td>59.28</td>
</tr>
</tbody>
</table>

C. Zeta Potential Measurement

According to the Fig. 4, showed that that the zeta potential values of LLP varied from 1.62 mV to 11.4 mV for pH 2.0–6.0. However for pH 8–12 the zeta potential values is -34 mV -25mV. The charge of surface of a biomass related on dissociation acid–base of its functional groups [24]. So it established that modified LLP is weak acid cellulotic materials. The zeta values of LLP have become negative when pH increases due to separation of acidic functional groups. So it found that biomass negative site pH more than 8. The negative value of zeta potential value related with adsorption capacity of LLP. Therefore, zeta potential became more negative with increase in pH and adsorption capacity also.

The surface charge of Leucaena leucocephala pods has a negative surface charge resulting from the separation of hydrogen ions (H⁺) to form R-COO⁻ [25] according to Eq (2) and Eq (3)

\[
R-\text{COOH} = R-\text{COO}^- + H^+ \quad (2)
\]

\[
R-\text{OH} = RO + H^+ \quad (3)
\]

The highest value of negative of LLP appear at pH 8, so it is a favorable for positive metal ion through attraction on the active sites which form an electrostatic interaction. This is due to functional group that form after deprotonated and negatively charged. The functional groups include carboxyl, carbonyl, hydroxyl and other anionic ligands that interrelate with copper metal ion through adsorption at surface of LLP is confirmed negatively charged [25]. So it shows that as higher pH values that have negativity value on surface on sorbent, thus, the greater the level of adsorption of the metal.

D. Point Zero Charge pH (pHpzc)

To verify the adsorbent surface charge, determining the pH with a net total point at zero charge (pHpzc) is one of the parameter that important to count on as it can affect the adsorption capacity. Based on pH_{pzc}, it can define the relationship between pH of adsorption of heavy metals on sorbent surface such of LLP and also to determine the surface of adsorbent is negatively or positively charged [26]. Fig. 5 showed, the point zero charge is at pH 6 so bio-sorption of Cu (II) would be higher as reported by [12]. Furthermore, when pH below than point zero charge, (pH < pH_{pzc}) defines that positively charge on the adsorbent surface. However surface of adsorbent become negatively charged when it is above pH_{pzc} (pH > pH_{pzc}). The pH_{pzc} showed at 6, which is predominance due acidic groups on LLP surface, this is due to carboxylic and hydroxyl groups that have been discussed contain. [27] also stated that through the electrostatic force of attraction, negatively charged on the surface of the adsorbent would improves the adsorption capacity copper cations. Cu^{2+} and Cu (OH)_{2} ions are the main classes of metal ions in metal solution. Therefore, had electrostatic repulsion between copper ions and positive charge of the surface of biomass at low pH. However at higher pH less competition between surface adsorbent charge and copper ions. This is due to the surface charge become negative. Therefore, LLP is a good adsorbent which it can remove very high quantity of copper ions that was found in this investigation which is 96.3% removal as shown in Fig. 6 compared to other pH solution.

E. Effect of pH

The various solution of initial pH from 2 to 12 was presented in Fig. 6. Adsorption of Cu (II) increased with increase in pH from pH 2-12 and attained maximum Cu(II) removal at pH 8 which is 96.3% removal. At low pH values, there is a decreasing in the number of negatively charged on surface sites on LLP and also an increase of number of positive charge because of an electronic repulsion. Furthermore, the lower adsorption of copper metal ion at acidic pH due to the repulsion between positive site and Cu(II) ion for adsorption. On the other hand, high adsorption of copper metal ion favor at high value of pH because of an...
increment number of negatively charged on surface sites through electrostatic attraction.

However, once pH became more basic (around pH 10), adsorption declines as metal hydroxides precipitate as shown in Fig. 6. [28] Also found the similar reason.

It has been shown that maximum sorption values for modified LLP was recorded at pH 8 which above (pH_pzc = 6.8). Maximum sorption is obtained at initial pH around 8 which is quite far from the pH_pzc (6.8). At optimum pH value (pH 8.0), the surface of modified LLP is negatively charged plausibly due to the dissociation of the −COOH groups and favorable to the adsorption of Cu^{2+} and Cu(OH)^{+} which are dominating species of the Cu (II) in the solution at pH 8.0.

Copper ion adsorbed on the surface of the LLP thu ion exchange mechanism as following equations:

\[ 2(\text{−RCOOH}) + \text{Cu}^{2+} \rightarrow (\text{RCOO})_2\text{Cu} + 2\text{H}^+ \]  
\[ \text{−RCOOH} + \text{CuOH}^{+} \rightarrow (\text{RCOO})\text{CuOH} + \text{H}^+ \]  

(where −R represents the matrix of the LLP). In addition, the HCl was used to adjust the solution pH value.

The Cl^{-} added may result in a decrease of the free Cu^{2+} species and an increase in the formation of complex CuCl^{-}. This chloro-complex has larger molecular size than the free Cu^{2+} and is adverse to the bio-sorption, leading to a decrease in copper uptake [29].

Fig. 6. Effect of pH on adsorption capacity and percentage copper ions removal adsorption by LLP: C_{0} = 50 ppm, temperature = 25 °C

\[ \text{pH} \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12 \]
\[ \text{Concentration, ppm} \]
\[ \text{Without Adsorbent} \quad \text{With Adsorbent} \]

Fig 7. Effect of pH on the removal of Cu^{2+} with adsorbent and without adsorbent. C_{0} = 50 ppm, temperature = 25 °C, particle size 400 µm, contact time = 24 h, dosage = 0.25g

F. Effect of contact time

The contact time parameter for the adsorption of copper metal (II) on LLP powder was investigated from 10 to 180 min. According to the Fig. 8 shown below, the contact times at 80 min almost to be stable and constant. Meanwhile, from the 120 – 180 min of contact time, there is an excessive number of active sites on the surface of adsorbent that represent the highest percentage in adsorption of copper metal. Thus, the copper metal removal capability of LLP increased within the contact time. This leads the accumulation of heavy metal in the pore of active sites and begin offering resistance to diffusion of accumulated copper metals ions in the adsorbents.

The higher rate of metal removal from Leucaena for adsorption process causing a surface area on Leucaena pods becomes larger thus, the rate of adsorption also increases. It may because of the pore diffusion of copper metal on the adsorbent bulk [30]. According to the [31], the equilibrium process of using modified banana peels at 300 minutes, therefore, the adsorption process using the Leucaena leucocephala pods was efficient since it need just a few time to reach equilibrium state.

Fig. 7. Effect of time on the biosorption of copper ions by LLP: C_{0} = 50 ppm, particle size 400 µm, contact time = 180 min, temperature = 25°C, pH = 8 for Cu (II)

G. Effect of sorbent dosage

The effect of adsorbent dosage on copper ions removal is shown in

Fig. 8. The sorbent dosage is varies from 0.5 g to 1.0 g and keep constant others parameter such as initial concentration which is 50 mg/L, at room temperature (25°C), contact time (24 hours), and pH (pH 8) for the sorption of copper metal on sorbent pods. The equilibrium adsorption, q decrease when the dosage of adsorbent rises from 0.05g up to 0.5g in 250 mL of test solution and became constant from 0.5g to 1.0g. The best condition for adsorbent dosage shown is 0.75 g because there is more accessibility of binding sites on the adsorbent surface for a complexation of copper metal ions.

Significant improvement in adsorption will not happen if there is a further increase in adsorption dosage. This is due to no more available sites for adsorbent contact with copper ions and the site are saturated. Ref [32], also found that removal efficiency of modified sugarcane bagasse increases by increasing the adsorbent dosage. As a result, the removal of a given amount of solute can be
accomplished with greater economy of adsorbent [33].

Fig. 8. Effect of adsorbent dosage on of Cu (II) by LLP: C0 = 50 ppm, particle size 400 μm, contact time = 4 h, temperature = 25°C, pH = 8 for Cu (II)

IV. CONCLUSION

The effectiveness of the Leucaena leucocephala pods as a promising adsorbent is proven as the Cu (II) are removed. Based on the results obtained, Cu (II) is depending on the adsorbent dosage, contact time and pH. From the batch studies it was found that 0.75 g Leucaena leucocephala pods adsorbent has shown the maximum removal in removing lead ion which is 97.6 % compared to other adsorbent’s type and dosage. The best optimum condition for this adsorbent to remove copper (II) ion from solution is at pH 8 with 0.75g of dosage and reached equilibrium at 80 minutes. Hence, this treatment process quite economical and time saver. From this present study, it can be concluded that modified Leucaena leucocephala pods can be effectively in removal of copper (II) ion in aqueous solution

REFERENCES


**AUTHORS PROFILE**

**Noor Harliza Abd Razak** has received his Bachelor of Engineering in Chemical (B.Eng (Hons) Chemical) 2009 and Master Science (Chemical Engineering) by research 2007 from Faculty of Chemical Engineering, Universiti Teknologi Mara (UiTM). She is working as a senior lecturer in Faculty of Chemical Engineering, Universiti Teknologi Mara (UiTM). Her research interests are adsorption, waste water and lubricating oil.

**Nur Amalia Zulkepli** has received his Bachelor of Engineering in Chemical (B.Eng (Hons) Chemical) 2019.

**Juferi Idris** has received his Bachelor of Engineering in Chemical (B.Eng (Hons) Chemical) 2003 and Master Science (Chemical Engineering) by research 2007 from Faculty of Chemical Engineering, Universiti Teknologi Mara (UiTM). He also received PhD (Energy Engineering) Kyushu Institute of Technology, Japan. He is working as a senior lecturer in Faculty of Chemical Engineering, Universiti Teknologi Mara (UiTM) Cawangan Sarawak.