



## REMOVAL OF COPPER (II) IONS FROM AQUEOUS SOLUTION USING NEPHELIUM LAPPACEUM L. AS LIGNOCELLULOSIC BIOSORBENT

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### ABSTRACT

Rambutan (*Nephelium Lappaceum* L.) wood was found out as an alternative biosorbent of heavy metals. This study is to determine the effectiveness of rambutan wood as biosorbent to treat heavy metal contaminated wastewater. Nowadays, there are many conventional adsorbents prepared using chemicals or high cost methods to remove heavy metals from aqueous solution, however they have limited range of usage. Rambutan wood was collected from trunk of matured trees and thoroughly washed to minimize contaminant during the experiment and finally oven dried at 80 °C for 24 hours. The characterization of the biosorbent was performed using Fourier Transform Infrared (FTIR) Spectroscopy. The selected metal solution is copper (II), concentration  $1000 \pm 2 \text{ mgL}^{-1}$  was diluted to desired concentration. The parameters involved in this study are pH, mass of rambutan wood, contact time and initial metal ion concentration. The biosorption experiment was performed between pH: 2-6, contact time: 30-120 min, quantity of rambutan wood: 0.5 g-2.0 g, initial copper (II) concentration: 2, 4 and 6 ppm. The percentage of Cu (II) ion removal was analysed using atomic absorption spectroscopy (AAS). The best operating condition was found at pH 6, at period 60 min, with the amount of 2.0 g and at initial copper (II) concentration of 6 ppm. It has been shown that rambutan wood is highly effective in removing heavy metal from aqueous solution.

**Keywords:** adsorption, heavy metal, rambutan wood, uptake.

### INTRODUCTION

Nowadays, environmental pollution, specifically water pollution that causes by excessive discharge of heavy metal and mining of metal such as copper is causing a serious environmental and health issue worldwide. These heavy metals do not degrade into harmless end products but they give a serious effect in aquatic plants and animals [1]. The priority of maintaining suitable water quality standards for the environment and human health is importance by removing heavy metals from contaminated wastewater such as mining industry [2]. Therefore, it is necessary to treat the heavy metal contaminated wastewater to prevent further problem regarding environment and health. Although many conventional method have been used to treat heavy metal in wastewater which include precipitation, ion exchange and electrochemical technique treatment [3], but they have disadvantages which involves high operation cost and can cause other pollution if it involves using chemicals.

Recent decades has been reported that using biomass in biosorption method were effective and efficiently greatly in removing heavy metals. Woody plant waste is one of type of bio- wastes on which little attention has been given as stated by [4]. Other than that, pine bark and needles [5], sawdust [6] and petiolar felt-sheath of palm [7]. By using this method, less pollution of the environment, low cost of expenses and eco-friendly to the environment can be achieved. This is due to the properties of the *Nephelium Lappaceum* L. (rambutan) wood to be non-pollution for the environment, as it is mainly contain chemicals that consists of mainly fibres and protein which is advantageous for the environment. As rambutan wood can also easily obtain throughout the year, which can reduce the cost greatly. Due to the advantages, rambutan wood can be considered as new source of bio-adsorbents

that can be useful for copper removal from wastewater. In this study, rambutan wood was used as new biosorbent to explore its potential for removing heavy metals from heavy metal contaminated waste.

### METHODOLOGY

#### Biosorbent material

Rambutan wood was obtained from the cutting the trunk of matured trees. The trunk was debarked, cut into smaller pieces (2 cm x 2 cm), the soaked in boiling water for 30 min, thoroughly washed under tap water, and left for 3 hour in distilled water that was changed 3-4 times. The washed wood pieces were grounded into fibres, then, oven dried at 75 °C for 24 hours. The samples were characterized using Bruker, Fourier Transform Infrared (FTIR), model Tensor 27 with OPUS 6.0 software in order to show its appropriate transmittance of functional groups. The sample testing was carried out using Attenuated Total Reflectance (ATR) in powder form and scanned from 400 to  $4000 \text{ cm}^{-1}$ .

#### Batch biosorption

The biosorption were carried out in 100 ml flasks by transferring 100 ml of different concentrations of metal solutions for each parameters and 1 g of rambutan wood cubes. The flasks were shaken at 100 rpm for 60 min. The solution was separated by using filter. The residual metal ion concentrations was determined, from which was computed the quantity of metal absorbed by rambutan wood per gram. For the determination of pH on metal biosorption, pH from range 3-7 was equilibrated for the metal solution. For contact time, different periods between 30 and 120 min were set to allowed contact between metal solution and rambutan wood. The mass of rambutan wood



was varied between 0.5 g and 2.0 g to find out the best level of biosorption condition. As for the determination of initial metal ion concentration, ranged of concentrations used were 2, 4 and 6 ppm.

### Analytical procedure

Concentration of each metal in each parameter, the residue in each solution after biosorption was determined using AAS (Aurora Instrument).

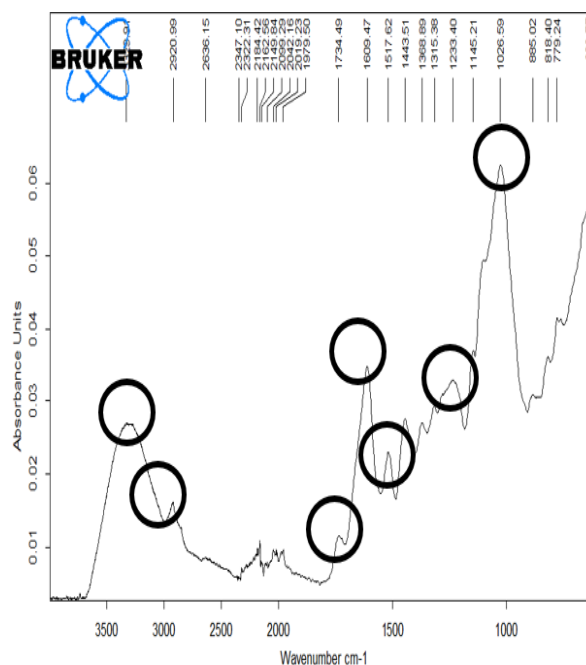
## RESULTS AND DISCUSSIONS

### Characterization of adsorbents

Fourier Transform Infrared (FTIR) Spectroscopy analysis (Figure-1) was carried out in order to identify the functional groups present in rambutan wood. According to previous findings [8], functional groups of adsorbents not only affect the adsorption behavior but also dominate the adsorption mechanism. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wavenumbers [9] as shown Table-1.

**Table-1.** Summarized of FTIR peaks.

Wavenumber (cm <sup>-1</sup> )	Assignment
1027	C=O stretching
1233	-SO <sub>3</sub> stretching
1517	Secondary amine group
1609	C=O stretching
2149	Amine group
2920	Aliphatic C-H group
3330	Bonded -OHgroup



**Figure-1.** FTIR spectrum of rambutan wood.

According to results that reported by previous studies[10] in the 1800-600 cm<sup>-1</sup> fingerprint area, specific and common bands appear, assigned to cellulose, hemicelluloses and lignin moieties which shows the characteristics of hardwood and softwood as shown in Table-2. The 1724-1736 cm<sup>-1</sup> band assigned to unconjugated keto  $\nu$  C=O in xylan remains very weak in softwoods, but well-defined in hardwoods that indicates that rambutan wood is a classified as softwood.

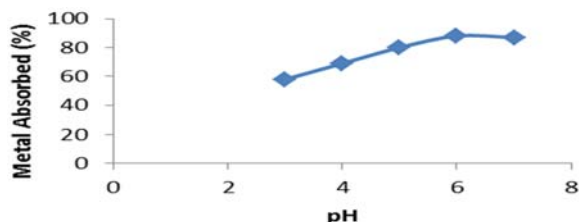
**Table-2.** Summarized of FTIR peaks of cellulose, hemicelluloses and lignin moieties.

Wavenumber (cm <sup>-1</sup> )	Assignment
1724-1736	unconjugated keto $\nu$ C=O in xylan
1594-1602	conjugated $\nu$ C=O
1510-1501	aromatic skeletal vibrations (total content of the lignin components)
1450-1456 and 1417-1424	$\delta$ C-H in lignin
1363-1370	$\delta$ C-H in cellulose and hemicelluloses
1320-1328	$\nu$ C-H in cellulose and $\nu$ C <sub>1</sub> -O of syringyl derivatives (characteristic of hardwoods)
1264-1270	vibrations of the guaiacyl rings and stretching vibrations of the C-O bonds (observed in softwoods)
1226-1234	syringyl ring vibration
1150-1156	$\nu$ C-O in lignin and xylan
1116	$\nu$ C-O-C in cellulose and hemicelluloses
1024-1034	$\nu$ C-O in cellulose and hemicelluloses
895-900	$\delta$ C-H in cellulose



### Effect of pH

Based on previous studies, pH of solution has been found as the most important variable for biosorption in this study. For obtaining the optimum pH or metal ion biosorption by rambutan wood, the removal of copper ion ( $\text{Cu}^{2+}$ ) from their aqueous solution was studied at different pH values. From the AAS analysis, at the pH 3 the biosorption of heavy metal is very low which is equal to 58%. The low metal biosorption at pH 3 is due to it start to attracting positively charged which is copper ion ( $\text{Cu}^{2+}$ ) and there is a competition between hydrogen ions ( $\text{H}^+$ ) and copper ions ( $\text{Cu}^{2+}$ ) and the winner can be calculated through the percentage removal of heavy metal [11]. A constant increase in the biosorption occurred in the pH range 4-5 (pH 4 is 69% and pH 5 is 80%). The percentage removal increased is due to pH increased from more acidic (pH 3) to less acidic (pH 7) region, the positive charged of solution is converted to negative charged (low competition between hydrogen ion ( $\text{H}^+$ ) and copper ion ( $\text{Cu}^{2+}$ )). Little increased at the pH 6 which is 88% and the graph showed the declining at the pH 7 which is 87% metal removed. From this trend, the optimum pH for rambutan wood to removed aqueous copper ion solution is pH 6 agrees with the previous findings [4]. For this reason, the percentage removal for above pH 7 was not investigated.

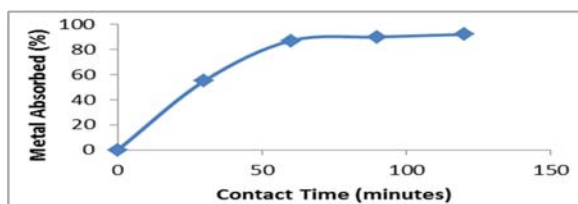


**Figure-2.** The effect of pH on the biosorption of copper (II).

### Effect of contact time

The contact time were studied on biosorption of copper by contacting 6ppm of metal solution at pH 6 with 1 g of rambutan wood. Copper shows that the sorption during the first 30 min was rapid increase, the sorption of copper is keep increasing until it's reached at the period of 60 min. During that period, the sorption of copper is at its best condition because after 60 min and above, there is less sorption of the copper. The phase for the sorption of the copper ion by the metal solution are being at slow rate phase because the best condition in removing the heavy metal from the solution are at the period of 60 min. The rapid stage for the sorption could last about several minutes until few hours. Meanwhile, the slow phase of the sorption may last for several hours until days [12]. The mass of rambutan wood been used to absorb copper ion is only 1g. If more rambutan is been used to absorb the copper ion for removal, it could lead to a more copper ion in the metal solution that contains more of the copper ion. The sorption of heavy metal such as copper as we use in our method is only best use at a period until 60 min. this period is the best condition for the rambutan wood to

absorb the copper ion, that contain in the metal solution with the copper ion.



**Figure-3.** The time-course relationship of the biosorption of copper (II).

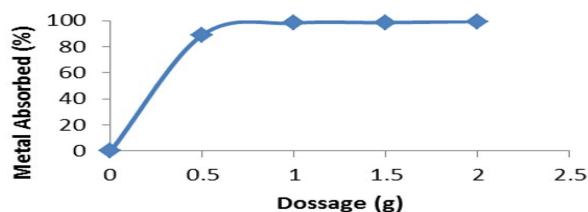
### Effect of biosorbent dosage

The quantity of rambutan wood was used between 0.5 g to 2.0 g in order to determine the optimum quantity of biomass needed for maximum sorption. Biosorption about 94.7% copper ion was achieved by using 0.5 g of rambutan wood. Further increases in the weight of rambutan wood were used which are 1.0 g, 1.5 g and 2.0 g resulted as 98.1%, 98.5% and 99.4% of metal absorbed respectively. The result shown that the optimum biosorption of 99.4% copper (II) was achieved when 2.0 g of rambutan wood biomass was used. The percentage of metal absorbed were obtained by increasing the quantity of rambutan wood biomass, while the concentration of copper ion and the solution volume were kept constant. The percentage of metal absorbed by rambutan wood was given in Table-3.

**Table-3.** Effect of quantity rambutan wood biomass on biosorption of copper (II) solution.

Dosage (g)	Concentration of metal absorbed (ppm)	Percentage of metal absorbed (%)
0	0	0
0.5	3.787	94.7
1.0	3.924	98.1
1.5	3.939	98.5
2.0	3.975	99.4

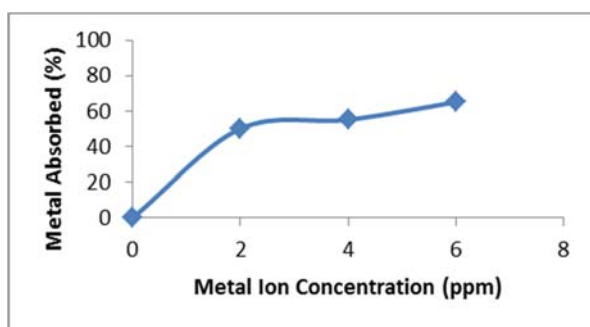
The increases in quantity of rambutan wood biomass lead to the increases of percentages of metal absorbed due to increase in the adsorption of surface area of rambutan wood [13]. The values of metal concentration at equilibrium also showed that increase in rambutan wood biomass strongly affected the removal of copper (II) from their aqueous solution. This was proven that lower equilibrium values indicating that as rambutan wood biomass was increased, the unoccupied sorption sites became more surplus with every increment of the biomass [4]. Therefore, as the mass of biosorbent increases, the percentages of metal removal increase.



**Figure-4.** The effect of increase of rambutan wood quantity (g L<sup>-1</sup>) on the biosorption of copper (II).

#### Effect of initial concentration

The concentration does affect the metal uptake mechanism because at low concentrations metal are absorbed by specific sites. When increasing the metal concentrations, the specific sites are saturated and the exchanges sites are filled thus the metal uptake mechanism is particularly dependent on the initial heavy metal concentrations (ppm) [14]. It is necessary to achieve the best condition for sorption data by using different metal solution ppm. For this purpose for 2, 4 and 6 ppm of copper (II) solutions at pH 6 were contacted with 1 g of rambutan wood. After the contact period of 60 min, the quantity of copper (II) absorbed per unit mass values were plotted. The results as shown in Figure-5, the most best condition for biosorption of metal solution was at concentration of 6 ppm is 65% which is where the specific sites of the biosorption reaches its most maximum uptake of metal. A similar trend has been observed for the biosorption of copper (II) on papaya wood and attributed the enhancement of metal uptake at lower metal ion concentrations that involves the specific sites being dependent on the initial heavy metal concentrations [4]. This concludes that suitable conditions of rambutan wood for the treatment of copper (II) metal solutions at lower concentrations (6 ppm).



**Figure-5.** The effect of initial metal ion concentration (ppm) on the biosorption of copper (II).

#### CONCLUSIONS

Rambutan wood has been proved to be highly effective for heavy metal absorption. One of the advantages of this biosorbent is its faster and high in the absorption rate. Besides that, rambutan woods are very easy to find throughout the whole year in Malaysia. Moreover, rambutan wood is very low cost as absorbent due to the abundance of the raw material around Malaysia.

This proved that this biosorbent could be used as a tool for the development of low-cost treatment of heavy metal waste.

#### ACKNOWLEDGEMENT

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