

## Biosorptive Removal of Cu(II) from Aqueous Solutions by Using *Carissa carandas* and *Syzygium aromaticum*

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**Abstract:** Biosorption of copper from aqueous solutions by *Carissa carandas* and *Syzygium aromaticum* was investigated in batch mode. Biosorptivity of both of these biosorbents has been correlated with the pH change, agitation time and dose of adsorbent and concentration of metal ions in the solution. Biosorbent *Carissa carandas* leaf powder showed higher sorption efficiency than that of biosorbent *Syzygium aromaticum* powder under identical experimental conditions. Also, the adsorption of Cu(II) onto *Syzygium aromaticum* was best described by the Langmuir isotherm model. The maximum adsorption capacities estimated from Langmuir isotherm model for Cu(II) were 54.2 mg/g and 76.61 mg/g for *Carissa carandas* and *Syzygium aromaticum* respectively.

**Keywords:** Green Chemistry, Heavy metals, Adsorption, Biosorption, *Carissa carandas*, *Syzygium aromaticum*, Langmuir isotherm, Freundlich isotherm

### Introduction

Heavy metals<sup>1</sup> are prior toxic pollutants existent in industrial wastewater, while they also constitute common groundwater contaminants. Many different definitions have been proposed for defining the heavy metals, some based on density, some on atomic weight or atomic number and some on chemical properties or toxicity. Ming-Ho<sup>1</sup> defined that heavy metal is the generic term for metallic elements having an atomic weight higher than 40.04u and heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water, such as cadmium (8.65), iron (7.9), lead (11.34), mercury (13.5). There are 92 elements which are occurring naturally, approximately 30 out of these metals and metalloids are potentially toxic to humans such as Be, B, Li, Ti, Al, V, Mn, Cr, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, Pt, W, Au, Hg, Pb and Bi. Living organisms also require some varying amounts of heavy metals like cobalt, copper, zinc, Iron, molybdenum and manganese but excessive levels of these metals can be damaging to the

organism<sup>2</sup>. As they pose serious environmental problems and are dangerous to human health, considerable attention has been given to the methods for their removal from industrial wastewaters<sup>1</sup>.

Researchers all over the world are doing tireless efforts to address this big 'issue' with best of their abilities and capabilities. We also contributed a large volume of work in last one and half decade in the field of water pollution, its prevention and remediation by adopting Green Chemistry principles<sup>3,4</sup>.

Green Chemistry plays a very important role and many green techniques including bioremediation, phytoremediation, photocatalytic processes, use of functionalized magnetic nanoparticles and use of alternative adsorbents produced by industrial and agricultural waste have been developed. Adsorption, a physicochemical process where the substance called adsorbate accumulates at the interface of solid called adsorbent, has become a useful green technique and attracts eyes of researchers worldwide and biosorption has certain advantages in this regard including low cost and high efficiency. However the major advantages of biosorption over conventional treatment methods include minimization of chemical and biological sludge, regeneration of biosorbent and possibility of metal recovery<sup>5</sup>.

Biosorption of metal ions is strongly affected by the properties of the water to be treated, such as pH, ionic strength, coexisting ions and suspended solids. Optimal pH for biosorption of metal cations is generally around neutral and their adsorbed amounts would decrease as solution pH is lowered because of diminishing of negatively charged sites on the biosorbents due to protonation. On the other hand, acidic pH favours biosorption of metal anions. Mine drainage and industrial wastewater usually contain more than one heavy metal species and these metal ions would compete with each other for the binding sites on biosorbents<sup>5</sup>.

In this era of rapid industrialization copper is one of the most common pollutants found in industrial effluents. Copper is commonly considered as micronutrient but at higher concentrations it is extremely toxic to living organisms and plants. It has many commercial uses because of its versatility. Copper is mainly used in making electrical wire, pipes, coins, valves, fittings, cooking utensils and building materials<sup>2</sup>. The main sources of copper pollution are fertilizer industry, metal cleaning and plating baths, paints and pigments, wood pulp production and the paper board mills<sup>6</sup>.

The World Health Organization (WHO) recommends a maximum acceptable concentration of Cu(II) as  $1.5 \text{ mg.L}^{-1}$  in drinking water<sup>7</sup>. The extreme consumption of copper leads to gastrointestinal problems, kidney damage, anaemia and lung cancer<sup>8</sup>. Copper is lethal for human in the range from 4 to 400 mg/kg of body weight<sup>9</sup>. Lower doses of copper ions can cause symptoms typical of food poisoning (headache, nausea, vomiting, and diarrhoea)<sup>10,11</sup>. In humans, the liver is the primary organ of copper-induced toxicity. Researchers reported copper toxicity causes Wilson's disease in humans<sup>12</sup>.

A number of methods for the removal of copper(II) from aqueous solutions are available, including chemical precipitation<sup>13</sup>, ion exchange<sup>14</sup>, adsorption, coagulation, oxidation or reduction, membrane filtration technology, reverse osmosis<sup>15</sup>, solvent extraction and evaporation<sup>2</sup>. However, these conventional methods have many disadvantages including incomplete metal removal, requirement of expensive equipment and monitoring systems<sup>1,3,16</sup>. As a result of the expensive nature of the use of the conventional methods, in recent years, attention has been focused on the potential of Green Chemistry for removal of copper from aqueous solution using adsorbents derived from low-cost materials. Many researchers have used

low-cost materials<sup>17</sup> as a viable biosorbent for copper(II) removal, namely, rice husk<sup>18-20</sup>, sugarcane, banana peel<sup>21-22</sup>, peanut shells<sup>23</sup>, activated sludge<sup>24</sup>, brewery biomass<sup>25</sup>, ipomoea carnea<sup>26</sup>, cassava<sup>27</sup>, tea waste<sup>28</sup>, fly ash<sup>29</sup>, tree fern<sup>30</sup>, cashew nut shell<sup>31</sup>, mansonie wood sawdust<sup>32</sup>, mushroom biomass<sup>33</sup>, activated carbon<sup>34-35</sup>, pomegranate pulp<sup>36</sup>, leaves of neem<sup>37</sup>, wheat straw<sup>38-39</sup>, sawdust (*Dalbargiasissoo*)<sup>40</sup>, pine fruit<sup>41</sup>, orange peel<sup>21,42</sup> and pine cone shell<sup>43</sup>.

In the present study *Carissa carandas* and *Syzygium arometicum* leaves were used for biosorption of copper(II) from aqueous solutions. Batch adsorption experiments were carried out at ambient temperature (300 K) as a function of solution pH (2-12), biosorbent dosage (20-100 g/L), contact time (60 min interval and up to 360 min), initial metal ion concentration and stirring speed (100-1000 rpm). Then, equilibrium isotherms and kinetic data parameters were evaluated.

## Experimental

*Carissa carandas* (better known as Karunda) belongs to *Apocynaceae* and is a rank-growing, straggly, wood, climbing shrub usually growing to 3-5 m high. Its leaves are evergreen, opposite, oval or elliptic, 2.5-7.5 cm long, dark green, leathery, glossy on the upper surface, lighter green and dull on the underside. It has fragrant flowers and green to purplish-red bitter juicy small fruits exuding flecks of latex<sup>44</sup>.

*Syzygium arometicum* (Cloves) are the aromatic dried flower buds of a tree in the family *Myrtaceae*, harvested primarily in Indonesia and Madagacar; it is also grown in Zanzibar, India and SriLanka. It is used as spice throughout Europe and Asia. The clove tree is an evergreen which grows to a height ranging from 10-20 m, having large oval leaves and crimson flowers in numerous groups of terminal clusters. Cloves are harvested when 1.5-2 cm long and consist of a long calyx, terminating in four spreading sepals, and four unopened petals which form a small ball in the center<sup>45,46</sup>.

The leaves of *Carissa carandas* and buds of *Syzygium arometicum* were collected from local field of Pushkar (India) and from local market of Jaipur (India), respectively. These were washed with distilled water, dried in sunlight, then 60 °C for 24 h in hot air oven. Finally, the dried leaves of *Carissa carandas* and *Syzygium arometicum* were grinded in clean electric mixer and stored in a dry and clean plastic bag.

## Instrumentation

The concentration of Cu(II) was determined by measuring the adsorption on the Atomic Absorption Spectrometer (Thermo Scientific SOLAAR S-series AA Spectrometer) at range 185-760 nm. The pH of the solution was measured with Toshniwal, CL54+ (range 0-14) pH meter. Analytical Scanning Electron Microscope, JEOL, JSM 6360A was used for scanning Electron Microscopy (SEM). Frontier Transform Infrared (FTIR) Spectrometer technique was used mainly to identify functional groups, that are capable of adsorbing metal ions. The spectra were collected by Shimadzu FTIR-8400 Spectrophotometer model with in the range 400-4000 cm<sup>-1</sup> using KBr window.

## Adsorption experiments and measurements

The stock solution of Cu(II) ion was prepared by dissolving 3.924 g of CuSO<sub>4</sub>.5H<sub>2</sub>O in 1000 mL volumetric flask and make up to the mark with double distilled water. All the required working solutions were prepared by diluting the stock solution with double distilled water. Batch adsorption studies were performed at room temperature. The adsorption equilibrium experiments for Cu(II) solution were carried out by taking 100 mL of copper solution in 250 mL

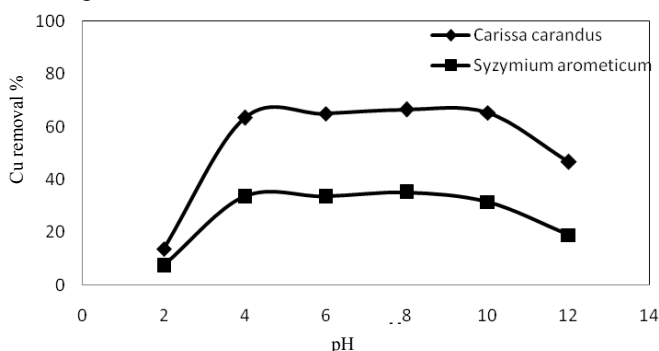
conical flask. After a defined time interval of 60 min., samples were withdrawn from the shaker, filtered by Whatman filter paper No. 1 and the supernatant solutions were analysed for Cu(II) ion concentration using an Atomic Absorption Spectrometer (Thermo scientific Solar S-series AA Spectrometer).

## Results and Discussion

### *Effect of solution pH on biosorption*

The pH has been identified as one of the most important parameter that is deciding one for metal sorption, because it is directly related with the competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface<sup>43</sup>. Therefore, preliminary experiments have been performed to find out the optimum pH for maximizing the copper removal. The effect of pH on the biosorption of Cu(II) ion onto *Carissa carandas* and *Syzygium aromaticum* powder were studied at various pHs ranging from 2 to 12 and the results are presented in Figure 1. From the figure it is observed that percentage adsorption of copper increases with the increasing pH of the system up to pH 8. The maximum biosorption was observed at pH 8.0 for *Carissa carandas* and *Syzygium aromaticum* both. The biosorption mechanisms on the *Carissa carandas* leaves and *Syzygium aromaticum* powder surface reflect the nature of the physicochemical interaction of the solution. At highly acidic pH (pH < 2.0), the overall surface charge on the active sites became positive and metal cations and protons complete for binding sites on cell wall, which results in lower uptake of metal and results in decrease adsorption. Also, at acidic pH, the adsorbent surface becomes positively charged and this not favours uptake of Cu(II). But at higher pH (basic nature), adsorbent surface gets negatively charged and favour uptake of cationic copper(II).

The biosorbent surface was more negatively charged as the pH solution increased from 2.0 to 6.0. The functional groups of the *Carissa carandas* leaves and *Syzygium aromaticum* powder were more deprotonated and thus available for the metal ions.



**Figure 1.** Effect of solution pH on biosorption of Cu(II) by *Carissa carandas* and *Syzygium aromaticum* ( $C_0 = 100$  ppm, dosage = 2 g/100 mL, Contact time = 180 minute,  $T = 300$  K)

Decrease in biosorption yield at higher pH (pH > 8) is not only related with the formation of soluble hydroxylated complexes of the metal ions but also to the ionized nature of the cell wall surface of the *Carissa carandas* leaves and *Syzygium aromaticum* powder under the studied pH, due to their exhausted surfaces (Table 1).

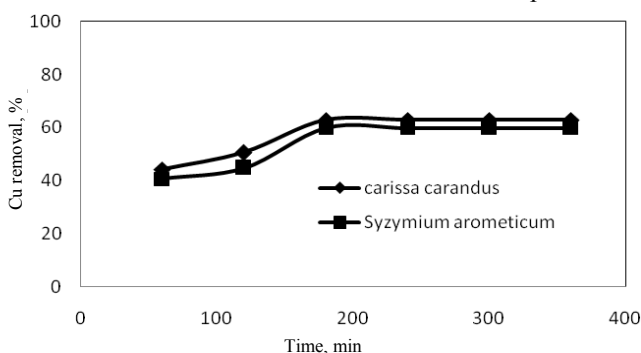
Similar results were obtained by Blazquez *et al.*,<sup>43</sup> which observed a sharp increase in the copper removal (from 25.3% to 73.3%) by pine cone shell when the pH values of the solutions changed from 3 to 6.

**Table 1.** Effect of solution pH on biosorption of Cu(II) by *Carissa carandas* and *Syzygium aromaticum* ( $C_0 = 100$  ppm, dosage = 2 g/100 mL, contact time = 180 min,  $T = 300$  K)

S. No.	pH	Removal of Cu(II), %	
		<i>Carissa carandas</i>	<i>Syzygium aromaticum</i>
1	2	13.77	7.37
2	4	63.36	33.50
3	6	64.95	33.50
4	8	66.51	35.22
5	10	65.3	31.5
6	12	46.62	19.0

*Effect of contact time on biosorption*

The rate of biosorption is important for designing batch biosorption experiments. As shown in Figure 2, the biosorption efficiency of Cu(II) increased considerably until the contact time reached 180 min. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 180 minutes for further experiments.

**Figure 2.** Effect of contact time on biosorption for Cu(II) by *Carissa carandas* and *Syzygium aromaticum* ( $C_0 = 100$  ppm, dosage = 2 g/100 mL, pH = 4,  $T = 300$  K)

The copper(II) adsorption rate at the initial stage (first 200 mins) may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. In this later stage, no sorption takes place due to non-availability of sorption sites. The equilibrium time was independent of adsorbent type. Therefore, further experiments were carried out at 60 min as a significant contact time for Cu(II) adsorption (Table 2).

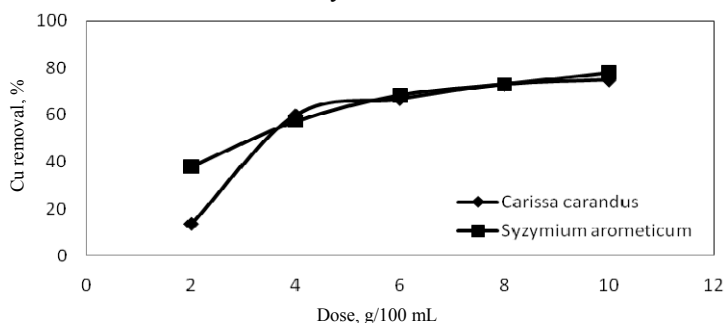
**Table 2.** Effect of contact time on biosorption for Cu(II) by *Carissa carandas* and *Syzygium aromaticum* ( $C_0 = 100$  ppm, dosage = 2 g/100 mL, pH = 4, temp = 300 K)

S. No.	Contact time, min	Removal of Cu(II), %	
		<i>Carissa carandas</i>	<i>Syzygium aromaticum</i>
1	60	44.27	40.73
2	120	50.64	44.84
3	180	62.89	59.94
4	240	62.89	59.94
5	300	62.89	59.94
6	360	62.89	59.94

### Effect of biosorbent dosage on biosorption

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration<sup>43</sup>. To investigate the effect of biosorbent dosage on biosorption, the experiments were conducted with constant copper concentration (100 mg/L) and samples with different biosorbent dosages ranging from 20-to 100g/L were used under the constant temperature and pH 4.

As shown in Figure 3 it was observed that percentage of copper(II) adsorption increased with increase of adsorbent dose for both adsorbents. This is mostly due to an increase in the adsorption surface area and the availability of more active and available sites.



**Figure 3.** Effect of biosorbent dose on biosorption capacity of Cu(II). ( $C_0 = 100$  mg/100mL, Contact time = 180 minute, pH = 4, T= 300 K)

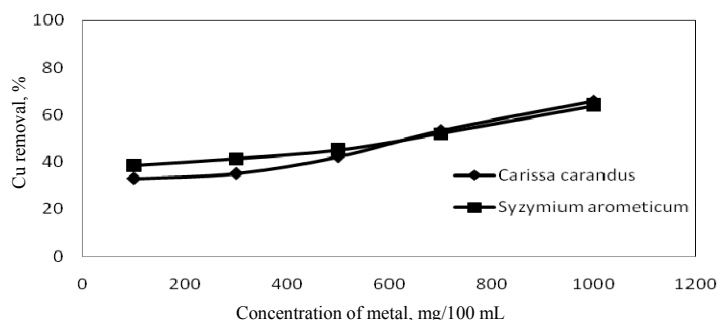
This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. Moreover, the maximum biosorption, 74.75% and 77.89% for *Carissa carandas* leaves and *Syzygium aromaticum* respectively were attained at biosorbent dosage, 10 g/100 mL. Therefore, the optimum biosorbent dosage was taken as 10 g/100 mL for further experiments for both biosorbents (Table 3).

**Table 3.** Effect of biosorbent dosage on biosorption capacity of Cu(II). ( $C_0 = 100$  ppm /100 mL, contact time = 180 minute, pH = 4, T= 300 K)

S. No.	Biosorbent g/100 mL	Removal of Cu(II), %	
		<i>Carissa carandas</i>	<i>Syzygium aromaticum</i>
1	2	13.77	38.14
2	4	59.89	57.23
3	6	66.78	68.39
4	8	72.86	73.04
5	10	74.75	77.89

### Effect of initial metal concentration on biosorption

Figure 4 shows the trends in the metal ion adsorption at different initial metal concentrations. It was observed that the amount of metal ion adsorbed increased as the initial metal concentration increased. For example, at an initial concentration of 100 to 1000 mg/L, the amount of Cu(II), adsorbed by *Carissa carandas* leaves and *Syzygium aromaticum* increased from 32.97% to 65.94% and 38.42 to 63.87% respectively. The solution contains more ions at high concentration, inducing a steep concentration gradient from the bulk of liquid to the surface of adsorbent. Thus, more ions diffuse to fixed available binding sites, causing more ions adsorbed per mass of adsorbent (Table 4).



**Figure 4.** Effect of initial metal concentration on biosorption of Cu(II), (Dosage = 2 g/100 mL, contact time = 180 minute, pH = 4, T = 300 K)

**Table 4.** Effect of initial metal concentration on biosorption of Cu (II). (Adsorbent Dosage = 2 g/100 mL, contact time = 180 minute, pH = 4, T= 300 K)

S. No.	Concentration of metal, mg/100 mL	Removal of Cu(II), %	
		<i>Carissa carandas</i>	<i>Syzygium aromaticum</i>
1	100	32.97	38.42
2	300	35.16	41.34
3	500	42.2	45.07
4	700	53.33	52.08
5	1000	65.94	63.87

These results are in good accordance to those obtained by other researches studying the copper biosorption on different biomaterials<sup>43,47-55</sup>.

### *Isothermal studies*

Adsorption isotherms describe how the adsorbate interacts with adsorbent and show the comprehensive information about the nature of interaction. The analysis of the isotherm data by fitting them to different isotherm models is an important step to get information on the surface properties of the adsorbents and its affinity with copper. Find the suitable model that can be used for design purpose. In this research, biosorption isotherm study was carried out on two well-known two-parameter isotherms: Langmuir and Freundlich. The well-known expression of Langmuir isotherm model<sup>56</sup> is presented as:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (1)$$

Where,  $C_e$  (mg/L) and  $q_e$  (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively, and  $Q_0$  (mg/g) and  $b$  (L/mg) are the Langmuir isotherm constants.

According to Kratochvil and Volesky<sup>57</sup> high  $Q_0$  and  $b$  values correspond to good quality biosorbents. High values of  $b$  can be seen in an isotherm with a steep initial slope, indicating a high affinity of the sorbate for the sorbent. The well-known expression for the Freundlich isotherm model<sup>58</sup> is given as:

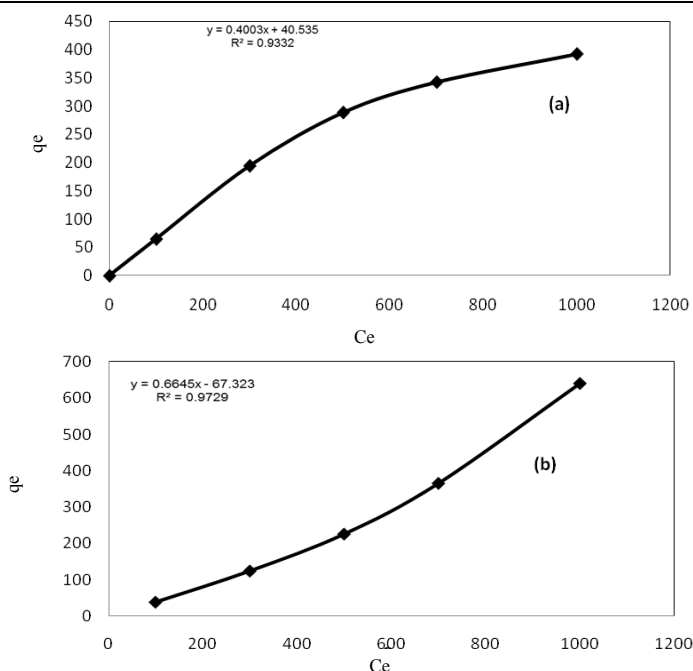
$$q_e = K_F C_e^{1/n} \quad (2)$$

Where,  $K_F$  (mg/g (L/g)<sup>1/n</sup>) is the Freundlich constant related to the bonding energy, 'n' is the heterogeneity factor which depicts the extent of deviation from linearity of the adsorption. It indicates the degree of non-linearity between solution concentration and adsorption (Table 5).

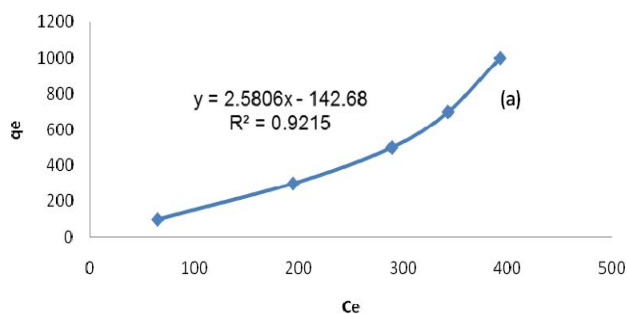
Table 5 lists the calculated Freundlich and Langmuir isotherm constants. For adsorption onto *Carissa carandas* leaves and *Syzygium aromaticum*, the adsorption of metal ion onto biosorbents was correlated well with the Freundlich isotherm model. The adsorption of Cu(II) onto *Syzygium aromaticum* was best described by the Langmuir isotherm model. The maximum adsorption capacities ( $Q$ ) estimated from the Langmuir isotherm model for Cu(II), were 54.21 mg/g and 76.61 mg/g for *Carissa carandas* leaves and *Syzygium aromaticum* respectively. The observations for Freundlich and Langmuir isotherms are shown in Figure 5 and 6 respectively.

**Table 5.** Langmuir and Freundlich isotherm constants for Cu(II) ion biosorption

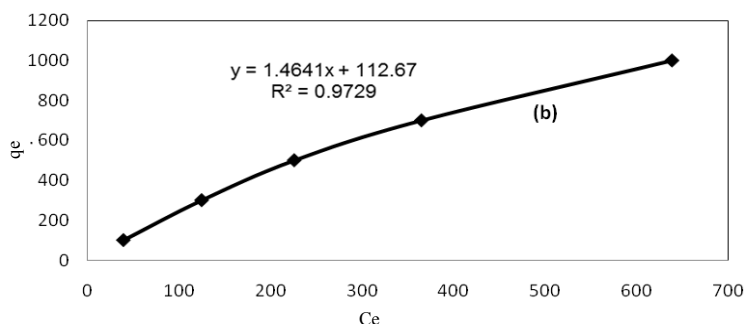
Adsorbent	Langmuir isotherm			Freundlich isotherm		
	$q_{\max}$	$K_L$	$R^2$	$K_F$	$n$	$R^2$
<i>Carissa carandas</i>	54.21	0.38	0.92	40.54	2.5	0.93
<i>Syzygium aromaticum</i>	76.61	0.68	0.97	67.32	1.5	0.97



**Figure 5.** Freundlich isotherm for (a) *Carissa carandas* and (b) *Syzygium aromaticum*







**Figure 6.** Langmuir isotherm for (a) *Carissa carandas* and (b) *Syzygium aromaticum*

Table 6 summarizes the comparison of Cu(II) adsorption capacities ( $q_m$ ) by various biosorbents *Carissa carandas* and *Syzygium aromaticum* present a good biosorption capacity, reflecting a promising future for its utilization in copper ion removal from aqueous solutions.

**Table 6.** Comparison of copper biosorption capacity (mg/g) by various biosorbents

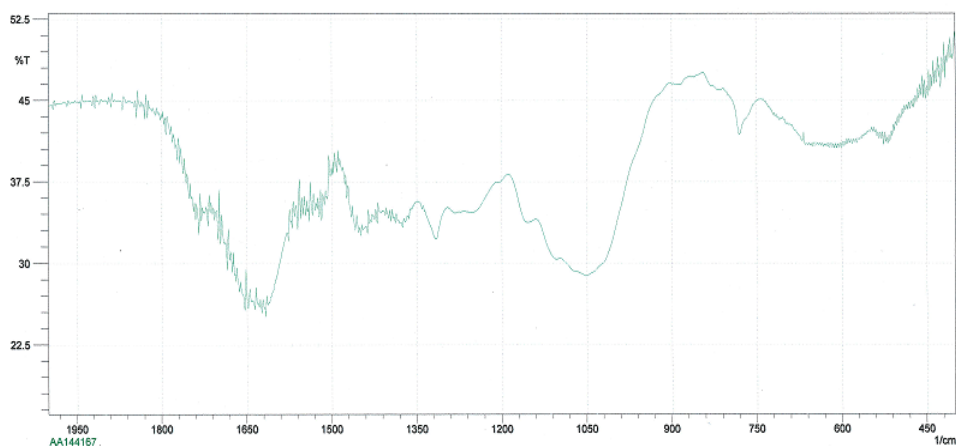
Biosorbent	$q_{max}$ , mg/g	Temperature, $^{\circ}$ K	pH	Reference
Pine cone shell	6.81	298	5	[43]
Cashew nut hell	20	303	5	[47]
Chestnut shell	12.56	293	5	[48]
	12.42	303	5	
	12.32	313	5	
	4.80	313	4.8	[49]
Eucalyptus Charcola	5.79	308	7	[50]
KOH treated pine cone powder	26.32	291	5	[51]
Natural clayey soil	4.41	310	5.5	[52]
Pomegranate peel	1.32	299	5.8	[53]
tamarind fruit nut testa	85.4	298	5	[54]
Pine cone powder	6.8	291	5	[55]
<i>Carissa carandas</i>	54.21	300	4	this work
<i>Syzygium aromaticum</i>	76.61	300	4	this work

#### FTIR analysis

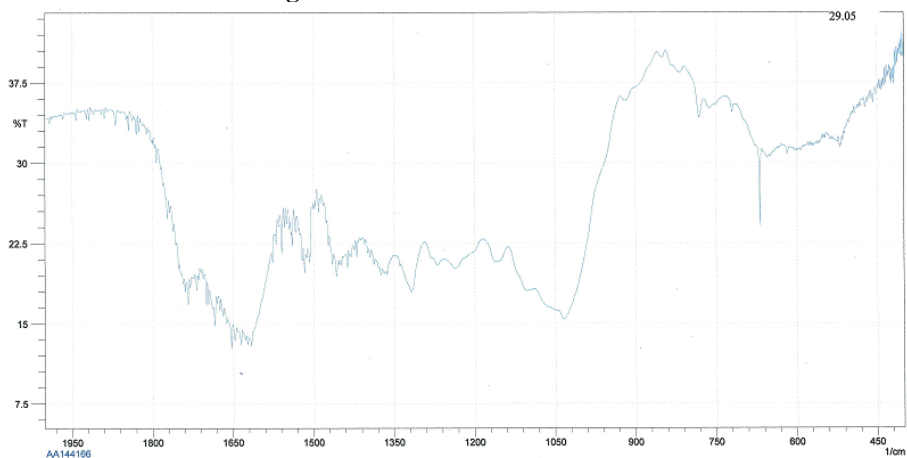
In order to determine the functional groups responsible for Cu(II) uptake by *Carissa carandas* was analysed using FTIR of *Carissa carandas* (Figure 7). The FTIR suggests the presence of –OH and –COOH groups in the said adsorbent and ensuring the possibilities of metal uptake by these functional groups. The peaks located at 1600-1660  $\text{cm}^{-1}$  are characteristics of carbonyl group stretching present in acidic group –COOH. The trough at 1050  $\text{cm}^{-1}$  is due to –C–O stretch for alcoholic group. Peak at 780  $\text{cm}^{-1}$  shows C–H stretching and peak at 1320  $\text{cm}^{-1}$  highlights C–C stretching. It seems well, according to the reported chemical composition of various compounds present in *Carissa carandas*<sup>59-61</sup>.

In order to determine the functional groups responsible for Cu(II) uptake by *Syzygium aromaticum* was analysed using FTIR of *Syzygium aromaticum* (Figure 8). *Syzygium aromaticum* contains 99.95% of essential oils. The major components are eugenol (87%), eugenyl acetate (8.01%) and  $\beta$ -Caryophyllene (3.56%)<sup>45</sup>. The FTIR suggests the presence of functional groups OH,  $\text{OCH}_3$  and  $\text{CH}_3\text{COO}$  with eugenolic unsaturation in the said adsorbent and ensuring the possibilities of metal uptake by these functional groups. Olefinic

unsaturation present may be due to C-C bending vibrations occur at very low frequencies ( $660\text{ cm}^{-1}$ ), while C-C stretching vibrations are weak and appear in the broad region of  $1010\text{--}750\text{ cm}^{-1}$ . The most informative bands in the spectra of aromatic compounds occur in the low frequency range between  $1000\text{--}800\text{ cm}^{-1}$ , which result from the out of plane bending of the ring C-H bonds. In plane bending bands appear in the  $1500\text{--}1200\text{ cm}^{-1}$  region. Skeletal vibrations involving C-C stretching within the ring absorb in  $1600\text{--}1510\text{ cm}^{-1}$ . The phenolic group shows a broad absorption band in  $900\text{--}750\text{ cm}^{-1}$  region because of out of plane bending of the bonded O-H group. An asymmetric C-O-C stretching band at  $1260\text{--}1200\text{ cm}^{-1}$  with symmetrical stretching near  $1100\text{ cm}^{-1}$  suggests the presence of  $\text{OCH}_3$  group.



**Figure 7.** FTIR of *Carissa carandas*



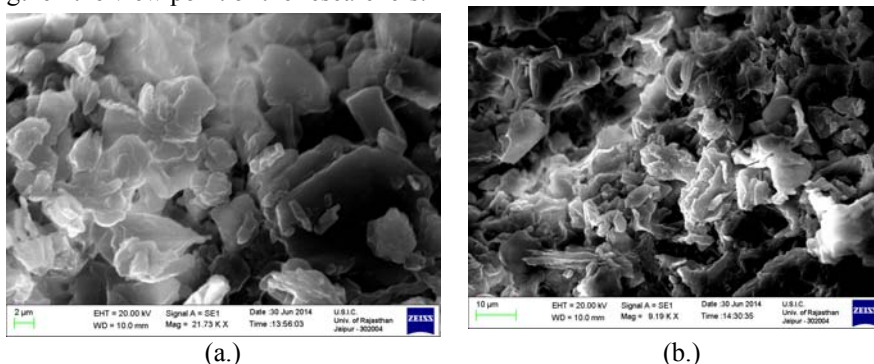
**Figure 8.** FTIR of *Syzygium aromaticum*

The whole FTIR discussion seems well, according to the reported absorption data of various expected groups present in *Carissa carandas* and *Syzygium aromaticum*<sup>62</sup>.

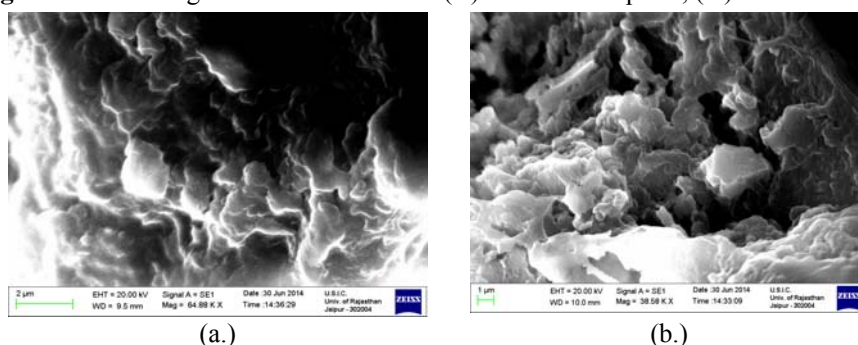
However, the exact functional groups, their nature, adsorption mechanism and sites of bonding between various functional groups present and  $\text{Cu(II)}$  ions are yet to be explored for better understanding of the whole story of this adsorption process, which we'll surely try to unfold in our future papers.

### SEM images

The SEM images of adsorbents before and after adsorption are given in Figure 9 and 10 respectively for *Carissa carandas* and *Syzygium aromaticum*. From these images, it is clear that there is significant difference in the appearance of the adsorbent surfaces. Images clearly highlight the action of adsorption on the surfaces of both the adsorbents and strengthen the view point of the researchers.



**Figure 9.** SEM image of *Carissa carandas* (a.) before Adsorption; (b.) after Adsorption



**Figure 10.** SEM image of *Syzygium aromaticum* (a.) before Adsorption; (b.) after Adsorption

### Conclusion

The present study focused on the use *Carissa carandas* leaves and *Syzygium aromaticum* powder as biosorbents for the removal of copper(II) from aqueous solutions. Biosorbent preparation, agitation, characterization and their uses for Cu(II) removal at different operating conditions are reported well.

Biosorbent *Carissa carandas* leaf powder showed higher sorption efficiency than that of biosorbent *Syzygium aromaticum* powder under identical experimental conditions. Also, the adsorption of Cu(II) onto *Syzygium aromaticum* was best described by the Langmuir isotherm model. The maximum adsorption capacities estimated from Langmuir isotherm model for Cu(II) were 54.21 mg/g and 76.61 mg/g for *Carissa carandas* and *Syzygium aromaticum* respectively.

However, we suggest that it is also necessary to investigate the efficacy of *Carissa carandas* leaves powder to treat real industrial effluents. There is a ready supply of agricultural wastes worldwide. The use of such materials will not only convert into low-cost effective adsorbents, but also provide a green solution to their disposal.

Since, several parameters including migration of metal ions from bulk solution to the surface of the adsorbent through bulk diffusion and the adsorption of metal ions at an active site on the surface of the adsorbent by chemical reactions play very important role in deciding the adsorption kinetics and adsorption mechanism; the actual adsorption mechanism is yet to be discussed and explained.

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