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Utilization of Mango Leaf as a Low-Cost Adsorbent for the Removal of Cu(II) Ions from Aqueous Solution

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The potential of mango leaves as a low-cost adsorbent for the removal of Cu(II) ions from aqueous solution was investigated in this study. The influences of pH, contact time, initial metal ions concentration, agitation rate and particle size were studied in batch experiments at room temperature. IR spectrum analysis was employed to study the functional groups of the mango leaves before and after modifications as well as after sorption process. Maximum sorption for metal ion was found to be at pH 5. The adsorption was rapid at the first 5 min of contact time and equilibrium was achieved in 60 min of agitation. Kinetic studies showed good correlation coefficient for a pseudo-second order kinetic model. The uptake was found to increase with higher agitation rate and smaller size of adsorbent. Langmuir and Freundlich, isotherm models were applied to describe the biosorption of Cu(II) ions onto mango leaves. Maximum sorption capacities calculated from the Langmuir model is 15.77 mg/g. The results showed that mango leaves have the potential to be applied as alternative low-cost biosorbent in the remediation of heavy metal contamination in wastewater.

Key Words: Mango leaves, Sorption, Heavy metal, Copper, Kinetics, Modelling.

INTRODUCTION

Heavy metals are member of a loosely-defined subset of elements that exhibit metallic properties, which mainly includes the transition metals, some metalloids, lanthanides and actinides. Certain heavy metals such as copper (Cu), is an essential micronutrient to human health. It plays a vital part in the development and performance of the human nervous and cardiovascular systems, as well as the skin, bone, immune and reproductive systems. Cu can also inhibit the growth of microbes, thus providing protection against harmful germs and bacteria in many environments.

Because of its distinctive physical properties by being malleable and ductile, a good conductor of both heat and electricity, Cu is heavily used in metal industries such as plating, mining and smelting, brass manufacture, electroplating industries, petroleum refining and excessive use of Cu-based agrichemical mining¹. Besides Cu, the increasing usage of other metals and chemicals in process industries and technological development, have resulted in generation of large quantities of effluent that contains high level of toxic heavy metals. Their presence poses environmental-disposal problems due to their non-degradable and persistence nature².

Most of the health disorders are linked with specific tendency of heavy metals to bioaccumulate in living tissues and their disruptive integration into normal biochemical processes³. For example, Cu, when being exposed at elevated levels, it can cause gastrointestinal disturbance, including nausea and vomiting. Long-term exposure to Cu could potentially leads to health problems such as headaches, stomachaches, dizziness and diarrhea.

Granular activated carbon has been the most popular adsorbent in wastewater treatment application throughout the world due to its highly porous texture and large capacity to adsorb pollutants. However, adsorbent-grade activated carbon is cost-prohibited and regeneration of the used carbon is not straightforward⁴. Therefore, attention has been intensified in the search for new and economical process that could remove heavy metals that are commonly used in the industry. In our continuing effort to apply the low cost materials for wastewater treatment, mango leaves have been selected and tested on its suitability to act as a potential adsorbent for the removal of Cu(II) ions from aqueous solution.

EXPERIMENTAL

Adsorbates: Cu(II) ion was used as the adsorbate in this study. A 100 mg/L Cu(II) stock solution was prepared by

dissolving accurately weight amount of copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) in deionized water. Appropriate dilution of the stock solution was carried out in order to obtain the desired concentration of Cu(II) solution used later in the experiment.

Adsorbents: Mango leaf was selected as adsorbent for removal of Cu(II) ion in this study. The leaves were obtained from a Chokanan mango tree located in local house yard at Sekinchan, Malaysia. Mature mango leaves were collected and each leaf was washed thoroughly under running tap water to remove dust and any adhering particles. The leaves were then dried under sunlight for a few days and then in oven at 80 °C until it became crisp. The dried leaves were crushed and blended to powder form using a blender. The mango leaves powder was boiled and washed for several times until it was free of colour and turbidity. Then, the powder was dried in oven at 80 °C overnight and stored in an airtight plastic for further use to avoid contact with moisture in atmosphere.

Batch experiments: Batch experiments were carried out at room temperature by shaking a mixture of 0.1 g of mango leaves powder and 20 mL of Cu(II) solution in a centrifuge tube, at agitation rate of 150 rpm for 2 h until equilibrium was reached unless otherwise stated. All samples were carried out in duplicate under the same conditions and the average results were taken. After agitation, the powder was removed by filtration using filter paper. The concentration of Cu(II) in the filtrates as well as in the control samples were determined by using flame atomic absorption spectroscopy spectrometer. Controls without adsorbent were simultaneously carried out to ascertain that adsorption was due to adsorbent and not the wall of the centrifuge tube. The uptake of Cu(II) was calculated using the following equation:

$$\% \text{Uptake} = \frac{C_o - C_t}{C_o} \times 100\% \quad (1)$$

where C_o is the initial concentration and C_t the concentrations at time t .

Effect of pH: The effect of pH on Cu(II) adsorption was studied by agitating 0.1 g of mango leaves powder and a series of 20 mL Cu(II) solution with concentration of 10 mg/L at different pH value, ranging from pH 2-10. The samples were agitated for 2 h to reach equilibrium and agitation speed was maintained at 150 rpm. The pH of Cu(II) solution was adjusted to the desired value by drop wise addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH) of various molarity.

Effect of initial metal ion concentration and contact time: The effect of initial concentration and contact time was investigated by agitating 0.1 g of mango leaves powder in 20 mL of 5 mg/L of Cu(II) solution over time periods of 5, 10, 15, 30, 60, 120, 180 and 240 min at constant agitation speed of 150 rpm. The above step was then repeated using 10 mg/L and 20 mg/L of Cu(II) solution respectively.

Effect of agitation: In this study, 0.1 g of mango leaves powder was agitated at 50 rpm in 20 mL of 10 mg/L of Cu(II) solution over time periods of 5, 10, 15, 30, 60 and 120 min. The above step was then repeated using agitation speed of 100 rpm and 200 rpm.

Effect of particle size: The effect of particle size was studied by using four different sizes of mango leaves powder,

which are <106 μm , 106-250 μm , 250-425 μm , 425 μm -1 mm. 0.1 g of mango leaves powder which were sieved into desired size was agitated at 150 rpm in 20 mL of 10 mg/L of Cu(II) solution over time periods of 5, 10, 15, 30, 60 and 120 min.

Sorption isotherm: The equilibrium isotherm was determined by using a range of different concentration of Cu(II) solution (10, 20, 30, 40, 50, 60, 70 and 80 mg/L). Mixture of 0.1 g of mango leaves powder and 20 mL of Cu(II) solution was agitated at the speed of 150 rpm for 4 h, which was sufficient to reach equilibrium. The amount of Cu(II) adsorbed at equilibrium (q_e) was calculated by using equation 2.

$$q_e = \frac{C_o - C_e(V)}{W} \quad (2)$$

where V = Volume of solution (mL), W = Weight of adsorbent used (g) and other terms are as previously defined.

RESULTS AND DISCUSSION

Fourier transform infrared analysis: FTIR analysis was carried out in order to identify the different functional groups present in mango leaves which were responsible for adsorption process. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wavenumbers. It was observed that the peaks at 3438, 2925, 1654 and 1057 cm^{-1} before adsorption had shifted to 3435, 2924, 1638 and 1065 cm^{-1} respectively. This was due to the participation of these functional groups in the binding of Cu(II) ions⁵. The comparison of band positions of various functional groups in mango leaves before and after Cu(II) ions adsorption was given in Table-1.

TABLE-1
COMPARISON OF FTIR BAND POSITIONS BEFORE
AND AFTER Cu(II) IONS ADSORPTION

Assignment	Wavenumber (cm^{-1})	
	Before adsorption	After adsorption
O-H stretching	3448	3435
C-H stretching	2925	2924
C=C stretching	1654	1638
C-O stretching	1057	1065

Effect of pH: pH of the aqueous solution is an important parameter governing the adsorption process as it not only affects the surface charge of adsorbents, but also influences the degree of ionization of metal ions in solution. The effect of solution pH on the adsorption of Cu(II) ions onto mango leaves was evaluated in the pH range of 2 to 10 and the result was showed in Fig. 1. At pH 2, Cu(II) ions uptake by mango leaves was the lowest, which was only 15.2 %. The uptake increased rapidly to 89.8 % at pH 3. At the pH range of 4 to 10, the uptake became almost consistent, ranging from 95.1 to 97.8 %. The maximum adsorption occurred at pH 5 and the uptake of Cu(II) ions was 97.8 %. The low uptake in acidic medium was due to the high concentration of H^+ ions which competed with Cu(II) ions for the adsorption sites. Besides, it is also suggested that at low pH, the carboxyl groups on the surface of mango leaves that were responsible for binding with Cu(II) were predominantly protonated ($-\text{COOH}$), hence incapable of binding Cu(II). As the pH increased, there were fewer H^+ ions present in the solution and consequently more negatively

charged sites were made available and this facilitated greater Cu(II) ions uptake by electrostatic attraction⁵⁻⁹.

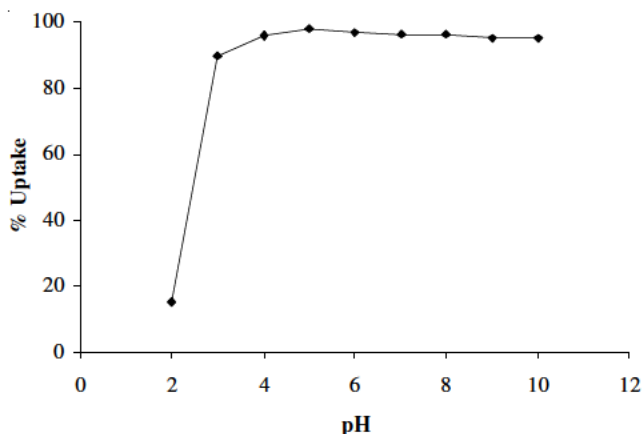


Fig. 1. Effect of pH on the uptake of Cu(II) ions by mango leaves

Effect of initial metal ion concentration and contact time: Fig. 2 shows the adsorption trend of Cu(II) ions onto mango leaves with increasing contact time and initial metal ion concentration. The plots revealed that a rapid uptake of Cu(II) ions occurred during the first 5 min of agitation, after which the rate of adsorption became slower and finally attaining equilibrium around 60 min. Thereafter, the contact time appeared to have a negligible effect on the uptake of Cu(II) ions. The observed fast initial uptake in the early stage of adsorption was due to the fact that most of the binding sites on mango leaves were free which allowed a quick binding of Cu(II) ions on the biomass¹⁰. As the binding sites became exhausted, the uptake rate slowed down due to competition for decreasing availability of active sites by metal ions. According to the test results, agitation time was fixed at 120 min for the rest of the batch experiment to ensure equilibrium was achieved. The plots of metal uptake as a function of time are single, smooth and continuous, suggesting the possibility of the formation of monolayer coverage of Cu(II) ions at the outer surface of adsorbent¹¹.

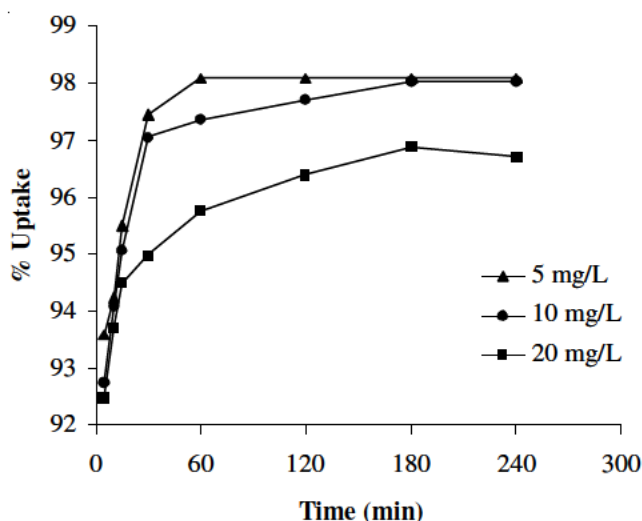


Fig. 2. Effect of initial metal ion concentration and contact time on the uptake of Cu(II) ions by mango leaves. ▲, ●, ■ – 5, 10 and 20 mg L⁻¹ of Cu(II) ions

Fig. 2 also showed that the uptake of Cu(II) ions decreased from 98.1% to 96.7% with the increment of initial Cu(II) ions concentration from 5 mg/L to 20 mg/L. It has been suggested that at lower metal ions concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption¹². When the concentration of Cu(II) ions became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites. However, the amount of Cu(II) ions adsorbed at equilibrium (q_e) actually increased from 0.8182 mg/g to 3.3048 mg/g with increasing initial Cu(II) ions concentration from 5 mg/L to 20 mg/L. A higher metal ion concentration resulted in a greater driving force to overcome the mass transfer resistance of Cu(II) ions between aqueous and solid phases. This will accelerate the probable collision between metal ions and sorbents, thus leads to a higher uptake of Cu(II) ions¹³.

Adsorption kinetic study: The study of adsorption kinetics in wastewater treatment is important as it not only provides valuable insight into the reaction pathways and the mechanism of sorption reactions, but also describes the solute uptake rate, which in turn control the residence time of sorbate uptake at the solid-solution interface¹⁴. The kinetics data obtained from adsorption of Cu(II) ions onto mango leaves was studied by using two common kinetic models, which are the pseudo-first order kinetic model¹⁵ and pseudo-second order kinetic model¹⁶.

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (\text{pseudo-first-order equation}) \quad (3)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (\text{pseudo-second-order equation}) \quad (4)$$

where q_e = the amount of Cu(II) ions adsorbed at equilibrium (mg/g), q_t = the amount of Cu(II) ions adsorbed at time t (mg/g), k_1 = the rate constant of pseudo-first order adsorption (1/min), h ($k_2 q_e^2$) = the initial adsorption rate (mg/g min) and k_2 = the rate constant of pseudo-second order kinetics (g/mg min).

It was found that the adsorption process of Cu(II) ions by mango leaves is better explained by pseudo-second order than the pseudo-first order model. The best fit model was selected based on the linear regression correlation coefficient (R^2), which is a measure of how well the predicted values from a forecast model match with the experimental data (Table-2). Besides, the equilibrium adsorption capacities determined from the first order kinetic model were lower than those determined experimentally. It thus appears that the system under study is more appropriately described by the pseudo-second order model which was based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electron between sorbent and sorbate¹⁶.

Effect of agitation rate: Agitation is an important parameter in adsorption phenomena as it influences the distribution of the solute in the bulk solution and the formation of the external boundary film¹⁷. The effect of agitation rate on sorption was investigated by conducting experiments at agitation rate of 50 rpm to 200 rpm at different time intervals. Fig. 3 shows the variation of Cu(II) ions uptake with agitation rate.

TABLE-2
PSEUDO-FIRST AND PSEUDO-SECOND ORDER KINETIC MODELS PARAMETERS FOR ADSORPTION
OF Cu(II) IONS ONTO MANGO LEAVES AT DIFFERENT INITIAL CONCENTRATIONS

Initial concentration (mg/L)	$q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
		$q_{e, \text{cal}}$ (mg/g)	k_1 (1/min)	R^2	$q_{e, \text{cal}}$ (mg/g)	k_2 (g/mg min)	h (mg/mg min)	R^2
5	0.83	0.07	0.081	0.980	0.82	4.288	2.870	1
10	1.59	0.06	0.023	0.846	1.60	1.469	3.731	1
20	3.30	0.12	0.018	0.954	3.31	0.677	7.391	1

It was observed that the percentage uptake increased when the agitation rate was increased. During the first 5 min, the uptake was 88.2, 92.8 and 96.4 % for the agitation rate of 50 rpm, 150 rpm and 200 rpm, respectively. A higher uptake under the influence of a greater agitation speed is due to lessen of boundary layer resistance to mass transfer surrounding the sorbent particles. In addition to that, higher agitation rate also spread the Cu(II) ions in the solution, providing better access to the active sites on adsorbent surface. A similar trend was observed for varying agitation speeds for the adsorption of Cu(II) and Pb(II) ions onto tartaric acid modified rice husk¹⁸.

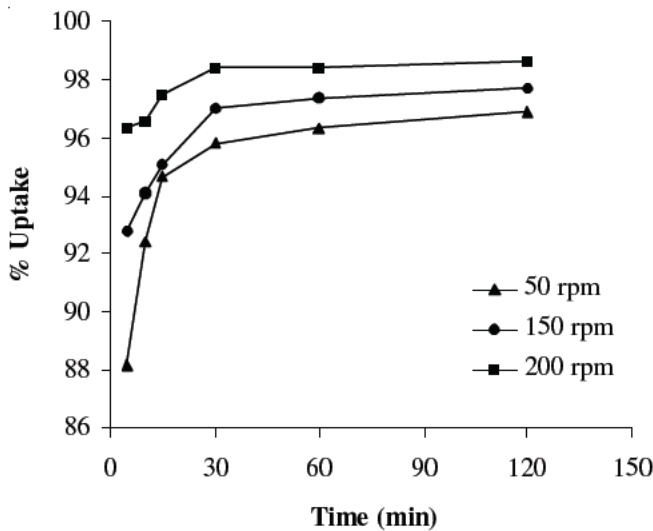


Fig. 3. Effect of agitation rate on the uptake of Cu(II) ions by mango leaves

Effect of particle size: Particle size of adsorbents is an important factor affecting the adsorption capacity as it influences the surface area of adsorbent. The effect of particle size on the adsorption of Cu(II) ions was investigated in the range of 106 μm^{-1} mm. Fig. 4 shows the variation of Cu(II) ions uptake with time for adsorbent of different particle sizes. The results indicated that the metal ions uptake increased with decreasing particle size. As can be seen, for the first 5 min of contact, the uptake increased from 91.3 % to 96.7 % when the particle size decreased from 425 μm^{-1} - 1 mm to < 106 μm . The higher uptake with decreasing particle size was attributed to the fact that smaller particles had larger external surface area compared to larger particles, hence more binding sites were exposed on the surface and thus, leading to higher adsorption capacity since adsorption is a surface process. Apart from that, particles with smaller size also moved faster in the solution compared to larger particles, consequently, the adsorption rate was faster. In a study involving the removal of Pb(II) ions using activated carbon prepared from coconut shell, the effect of particle sizes was investigated from 75 μm to 850 μm ¹⁹.

The authors found that the percent removal of Pb(II) ions increased from 42 % to 99 % as the particle size decreased from 850 μm to 75 μm for an initial concentration of 20 mg/L Pb(II) solution. Besides related the findings to the surface area, explanation has also been made based on diffusional resistance. For larger particles, the diffusional resistance to mass transport was higher and most of the internal surface of the particle might not be utilized for adsorption, hence, the amount of Pb(II) ions adsorbed was small.

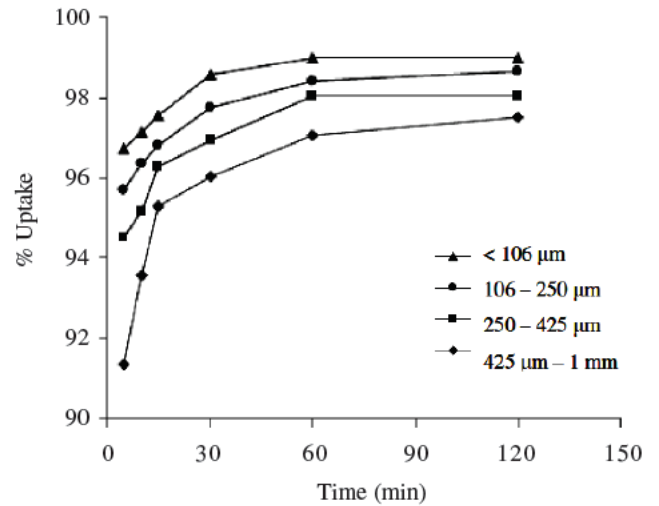


Fig. 4. Effect of particle size on the uptake of Cu(II) ions by mango leaves

Adsorption isotherm: Equilibrium adsorption data of Cu(II) ions onto mango leaves are fitted into both Langmuir and Freundlich equations. The linearized Langmuir model is written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (5)$$

whereas the linear form of Freundlich can be represented as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (6)$$

where C_e = equilibrium concentration of the Cu(II) ions (mg/L), q_e = amount of Cu(II) ions adsorbed at equilibrium (mg/g), q_m = maximum adsorption capacity (mg/g), K_L = adsorption equilibrium constant (L/mg), n = Freundlich constant for intensity and K_f = Freundlich constant for adsorption capacity. The linear plots of C_e/q_e versus C_e and $\log q_e$ versus $\log C_e$ for the adsorption of Cu(II) ions onto mango leaves are shown in Figs. 5 and 6, respectively.

The plot of C_e/q_e against C_e gave a straight line with a correlation coefficient of 0.9918, which was close to unity, thus indicating that the data conform well to the Langmuir isotherm model. In order to investigate the effectiveness of mango leaves as a potential adsorbent in removal of Cu(II)

ions, the value of the maximum adsorption capacity obtained in this study was compared with that from other reported adsorbents. As shown in Table-3, the Cu(II) ions adsorption capacity of mango leaves was 15.77 mg/g, which can be considered as comparable to other reported adsorbents.

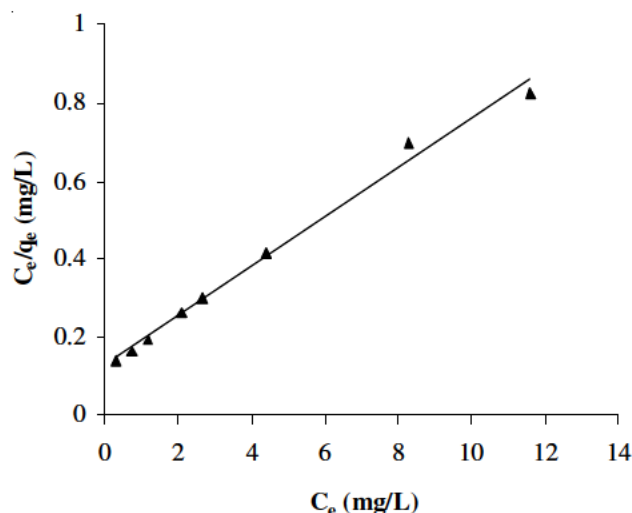


Fig. 5. Langmuir isotherm plot for the adsorption of Cu(II) ions by mango leaves

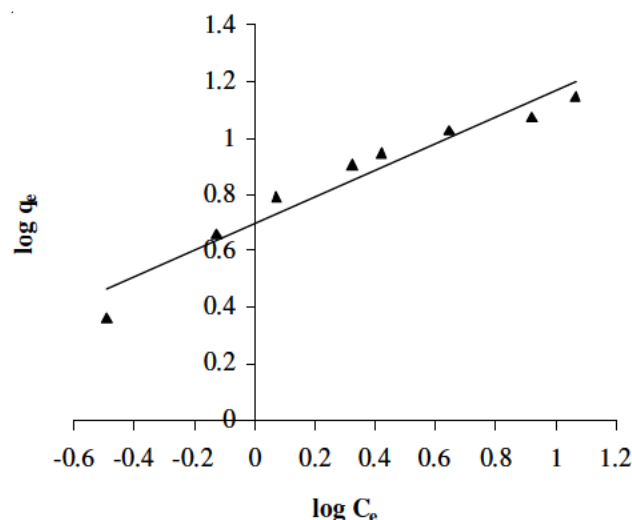


Fig. 6. Freundlich isotherm plot for the adsorption of Cu(II) ions by mango leaves

TABLE-3
COMPARISON OF Cu(II) IONS UPTAKE OF SELECTED
SIMILAR NATURE ADSORBENTS

Adsorbent	q_m (mg/g)	References
Peanut shell	25.39	20
<i>Cinnamomun camphora</i> leaves	16.76	21
<i>Tectona grandis</i> leaves	15.43	7
Spent grain	10.47	22
Rubber (<i>Hevea brasiliensis</i>) leaves	8.92	5
Cashew nut shell	20.00	23
Mango leaves	15.77	This study

The Langmuir parameters were also used to predict the affinity of the leaf powder surfaces towards the Cu(II) ions by using dimensionless separation factor, R_L , which was expressed in equation 7.

$$R_L = \frac{1}{1 + K_L C_o} \quad (7)$$

For all the concentrations under study, the R_L values obtained were in the range of $0 < R_L < 1$, which indicated a favourable isotherm shape for the adsorption of Cu(II) ions onto mango leaves.

Conclusion

The results of this study indicated that the uptake of Cu(II) ions by mango leaves was affected by pH, contact time, initial Cu(II) ions concentration, agitation rate and particle size. The optimum pH for adsorption of Cu(II) ions was found to be at pH 5. The uptake of Cu(II) ions increased with increasing contact time and decreasing metal ions concentration and equilibrium was attained in 60 min of contact time. The kinetic data obtained from this study fitted well with the pseudo-second order model. The maximum adsorption capacity determined from the Langmuir isotherm model was 15.77 mg/g.

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