



Reclamation of wastewater containing Cu(II) using alginate *Mentha spicata* biomass

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ABSTRACT

The task of looking for new and potentially feasible metal biosorbents has a wide scope. In the present work, optimization of thermodynamic and kinetic parameters has been carried out for the removal of Cu(II) from aqueous solution using *Mentha spicata* distillation waste (native and alginate) biomass. *M. spicata* distillation waste biomass was efficiently used for toxic Cu(II) removal under optimized conditions of pH, biosorbent dose, biosorbent size, initial metal concentration, contact time, and desorption. Langmuir adsorption isotherm and pseudo-second-order kinetic models fitted well to Cu(II) sorption by native and alginate *M. spicata* distillation waste biomass. The significant changes in the vibrational frequencies of Fourier transform infrared spectra implicated that carboxylic, carbonyl, and nitrile groups played vital role during Cu(II) biosorption process. A new peak at 1,735 cm⁻¹ corresponding to the –C=O groups appeared, suggesting that –C–O groups oxidized to –C=O groups during biosorption process. Alginate *M. spicata* distillation waste biomass exhibited a very high Cu(II) adsorption capacity (176.96 mg/g).

Keywords: Cu(II); *Mentha spicata*; Biosorption; FTIR; Immobilization

1. Introduction

Toxic heavy metals enter the food chain through drinking water (mostly ground water), agricultural

products, and sea foods. Due to accumulative behavior and toxicity, heavy metals have significant impact on health of human beings and animals consuming such commodities. Some heavy metals such as iron, cobalt, copper, manganese, molybdenum, and zinc are essential elements for life (at trace concentrations) and many

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are highly toxic like lead, cadmium, mercury, arsenic, chromium, copper, nickel, etc. [1]. Copper is found in natural deposits as ores along with other elements and also widely used in household plumbing material. Acute copper toxicity results in a number of pathologies and in severe cases causes death. Severe neurological defects and life diseases can result from chronic copper toxicity. Copper-induced damage is related with abnormal metabolism of copper and neurogenerative changes. Copper alloys are used in domestic water taps which result in the introduction of copper in food chain. Exposure to excessive levels of copper can result in a number of adverse health effects including liver and kidney damage, anemia, immunotoxicity, and even death. There is a strong evidence to suggest that Wilson's disease, Indian childhood cirrhosis, and possible idiopathic copper toxicities are caused by an increased susceptibility to Cu(II). Copper concentrations in the drinking water vary widely. Along with the manufacturing of the commercial appliances, it is also used as the copper sulfate pentahydrate for the control of algae. Copper concentration in the treated water often increases during distribution, particularly in the systems where an acidic pH exists or in the presence of high-carbonate waters with an alkaline pH. The current World Health Organization (WHO), Environmental Protection Agency (EPA), International Bottled Water Association (IBWA) drinking water standard for Cu(II) is 1.0 mg/L. Reclamation and reuse of water by wastewater treatment is essential due to increased pressure on water bodies. The conventional methods for the heavy metal removal from aqueous streams are reverse osmosis, electro-dialysis, ultra-filtration, ion-exchange, chemical precipitation, phytoremediation, and bio-reduction [2–4]. Major disadvantages of these methods are incomplete metal removal, generation of toxic sludge, or other waste products that need a careful disposal. These limitations made these methods expensive. Biosorption has emerged as an alternative to traditional physico-chemical methods. Biosorption commonly refers to the passive binding of metal ions or radioactive elements by dead biomass. Depending on the cells metabolism, biosorption may be classified into metabolism dependent and independent. Varieties of natural materials, particularly of cellulosic nature, have been considered as potential biosorbents for toxic heavy metals [5–9]. The task for looking the new and potentially feasible metal biosorbents has a wide scope. Biomass used may be living, such as seaweeds [10], bacteria [11], yeast [12], algae [13], moss [14], and non-living biomass such as crab shells [15], peat [16], cone biomass *Pinus sylvestris* [17], neem [18], orange residue [19], wheat shell

[20], dried stem [21], activated sludge [22], fruit waste [23], etc.

Biosorbents used should be easily available in large amounts in nature and must be cost effective. The use of freely suspended microbial biomass has disadvantages such as small particle size, low mechanical strength, and difficulty in separating biomass and effluent. The search for new eco-friendly technologies involving the removal of heavy metals from wastewaters has directed attention to biosorption [24]. *Mentha spicata* (common name spearmint) is one of the most important spice plants. In the present work, alginate *M. spicata* distillation waste biomass is used for Cu(II) uptake from aqueous solution. The present study was undertaken with the following objectives. (i) To study the use of *M. spicata* distillation waste biomass as a biosorbent for Cu(II); (ii) to investigate the effect of different experimental conditions such as pH, biosorbent dose, biosorbent size, initial metal concentration, time contact, desorption, column study; (iii) to evaluate the effects of different pretreatments on the uptake of Cu(II) by alginate *M. spicata* distillation waste biomass.

2. Materials and methods

2.1. Chemicals and reagents

The Analytical Reagent Grade chemicals used in the present work were purchased from Merck (Germany). Chemicals used were $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, CH_3COOH , CaCl_2 , H_2SO_4 , NaOH , HCl , Na_2SO_4 , MgSO_4 , ZnSO_4 , Al_2O_3 , $\text{S}_2\text{O}_8^{2-}$, H_3PO_4 , and Cu AAS Standard solutions. In order to prepare 1,000 ppm Cu(II) stock solution, 3.96 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 100 mL of deionized water (DW) and diluted up to 1,000 mL. Working standards of desired concentrations were prepared by adequate dilution of stock solution with DW.

2.2. Biomass collection, pretreatment, and immobilization

M. spicata distillation waste biomass used in the present study was collected from Rosa Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. There is no commercial significance of *M. spicata* distillation waste biomass left after essential oil extraction. The collected waste biomass after steam distillation of *M. spicata* was oven dried at 60°C for 24 h. To obtain adsorbent with a known particle size, *M. spicata* distillation waste biomass was sieved and stored in airtight jars. Immobilization of *M. spicata* distillation waste biomass was

done by following method: 100 mL of 2% sodium alginate was mixed with 1 g of waste biomass. The mixture was then stirred thoroughly. Uniform sized spherical beads were obtained by propelling out the mixture into 0.1 M CaCl_2 from 100 mL burette. The beads were preserved in airtight glass jar using 1 M solution of CaCl_2 as preservative. Physical and chemical pretreatments were carried out to evaluate the effects on Cu(II) uptake capacity of *M. spicata* distillation waste biomass. In physical pretreatment, 0.1 g of beads were heated in an electrical oven up to 60°C for 30 min. Beads were also physically modified by boiling 0.1 g of beads in 50 mL of DW for 30 min on a flame. Chemical pretreatments were done by soaking (for 2 h at 30°C) 0.1 g of beads in 50 mL (0.1 N) of HCl, H_2SO_4 , NaOH, acetone, and ethanol.

2.3. Batch biosorption studies

Experimental parameters included in the present study were pH (1.5, 2, 3, 4, 4.5, and 5), biosorbent dose (0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 g/100 mL), biosorbent size (0.250–0.350, 0.350–0.500, 0.500–0.710, and 0.710–1.00 mm), initial metal concentration (25, 50, 100, 150, 200, and 400 mg/L), column study and contact time (15, 30, 60, 120, 180, 360, 720, and 1,440 min). Aqueous medium's pH was adjusted by using 0.1 N solutions of NaOH and HCl [25–28]. Desorption of Cu (II) loaded on the waste biomass was studied by using EDTA, HCl, and NaOH. The copper uptake was calculated by concentration difference method. The initial concentration C_i (mg/L) and metal concentration at different time intervals, C_e (mg/L) were determined and metal uptake q_e (metal adsorbed/g of adsorbent) was calculated by mass balance equation (1):

$$q_e = (C_i - C_e) V / 1,000w \quad (1)$$

where V is the volume of solution in mL and w is the mass of sorbent (g), C_i is the initial concentration at the concentrations (mg/L) at the various time intervals and q_e is the metal uptake in (mg/g). The extent of sorption in percentage is found from the relation (2).

$$\text{Sorption (\%)} = (C_i - C_e) / C_i \times 100 \quad (2)$$

2.4. Metal analysis

Cu(II) contents in sample and control assays were determined using Flame Atomic Absorption Spectrophotometer (Perkin–Elmer AAnalyst 300) equipped with an air–acetylene burner and controlled by Intel

P-IV personal computer. The instrument was periodically checked by known standards to ensure accuracy. For each sample, three readings were taken and mean of these three was computed along with standard deviation for each sample. The amount of metal bio-sorbed on the waste biomass was assumed to be the difference between initial metal concentration and that present in the solution. Uptake was calculated by concentration difference method.

2.5. Fourier transform infrared (FTIR) analysis

The spectra were collected by FTS-135 (Bio-Rad) spectrometer after making KBr disc.

2.6. Statistical analysis

The data represents the mean of three independent experiments. All results were evaluated by mean \pm SD and Tukey's HSD test. All statistical analysis was done using Microsoft Excel 2007, version Office XP. The correlation coefficient (R^2) values of the linear form of Langmuir isotherm, Freundlich isotherm, pseudo-first-order, and pseudo-second-order models were also determined using statistical functions of Microsoft Excel, 2007 (version Office XP, Microsoft Cooperation, USA).

3. Results and discussion

3.1. Effect of pH

Effect of pH on Cu(II) biosorption is shown in Fig. 1. Cu(II) uptake capacity was maximum at pH 5.0 for both native and alginated biomass. However, Cu (II) uptake capacity (mg/g) of alginated biomass was

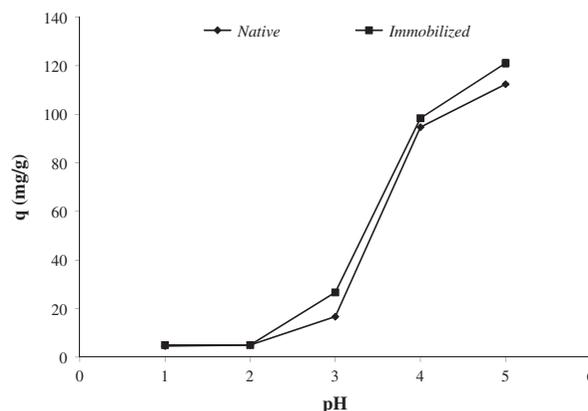


Fig. 1. Effect of pH on the uptake of Cu(II) by *M. spicata* distillation waste biomass.

greater than native biomass. Of physicochemical factors, pH seems to be the most important parameter in the biosorption process. It affects the chemistry of metals, the activity of the functional groups in the biomass, and the competition among metal ions [3]. The highest Cu(II) removal capacities were 112.40 and 121.60 mg/g, respectively, by native and alginate *M. spicata* distillation waste biomass. At low pH values, H^+ concentration is high in the solution which might increase the competition between H^+ and Cu^{++} for exchange sites on biomass. On increasing pH, $CuOH^+$ concentration increases rapidly and these ions adsorbed in larger amounts than Cu^{++} . Increase in Cu adsorption was also attributable to the hydrolysis reaction. The measured point of zero charge (pzc) of *M. spicata* distillation waste biomass was 6.17 with 0.1 M NaCl and 6.30 with distilled water. Because of the negligible difference of pzc between NaCl and pure water, the measured pzc was determined as 6.30.

3.2. Effect of biosorbent dose

Fig. 2 shows the effect of biosorbent dose on Cu(II) adsorption. Biosorbent dose was varied from 0.05 to 0.5 g while keeping the other parameters (pH 5.0, initial metal concentration (100 mg/L), biosorbent particle size (0.255–0.355 mm) at (30°C) constant. The results show that maximum biosorption by native, and alginate *M. spicata* distillation waste biomass occurred at 0.05 g/100 mL for Cu(II) solution was 114.60 and 122.06 mg/g, respectively. Uptake of Cu(II) decreased with increase of mass of *M. spicata* distillation waste biomass. The effect was marked for both native and alginate biomass. It was due to the interaction among cells that is caused by the interference between binding sites at higher concentrations.

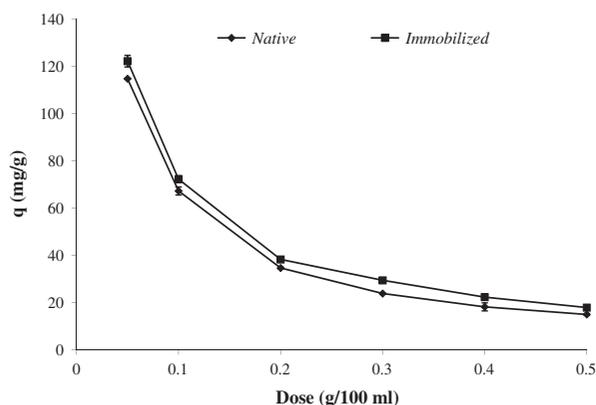


Fig. 2. Effect of biosorbent dose on the uptake of Cu(II) by *M. spicata* distillation waste biomass.

Availability of binding sites depends on the adsorbent dose added. Similar observations were made in the studies on metal sorption previously [26–28]. Thus, by using small batches of sorbent, more economical and efficient biosorption can be done.

3.3. Effect of particle size

Experimental data points obtained for the effect of biosorbent size on the uptake of Cu(II) by native and alginate *M. spicata* waste distillation biomass is given in Fig. 3. The maximum biosorption occurred with 0.255–0.355 mm adsorbent particle size for native and immobilized *M. spicata* distillation waste biomass. Increased total surface area at finer particle size created more sorption sites available for Cu(II) ions. Same effect was reported previously [26].

3.4. Effect of initial metal concentration

Effect of initial metal concentration on Cu(II) removal using native and alginate *M. spicata* distillation waste biomass is shown in Fig. 4. The data indicated that biosorption capacity increased with increase in the metal ion concentration. Maximum Cu(II) adsorption, 140.30 and 176.96 mg/g was observed at initial metal concentration of 400 mg/L by native and alginate biomass, respectively. The results indicated that surface saturation was dependent on the initial metal ion concentrations. However, at high concentrations, Cu(II) diffused at a slower rate. It has also been noted that percentage removal of Cu(II) was higher at lower concentrations.

Modeling of equilibrium data is fundamental for industrial application of biosorption as it gives

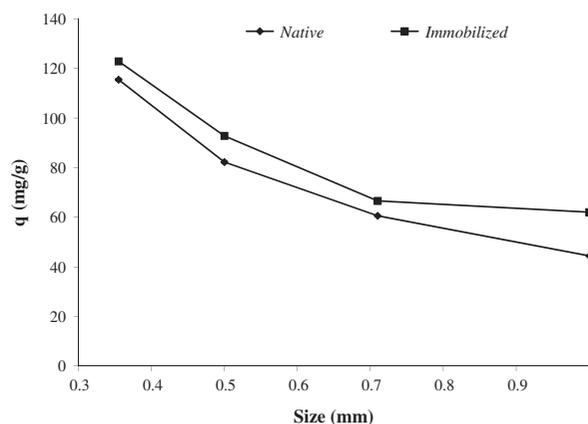


Fig. 3. Effect of size on the uptake of Cu(II) by native *M. spicata* distillation waste biomass.

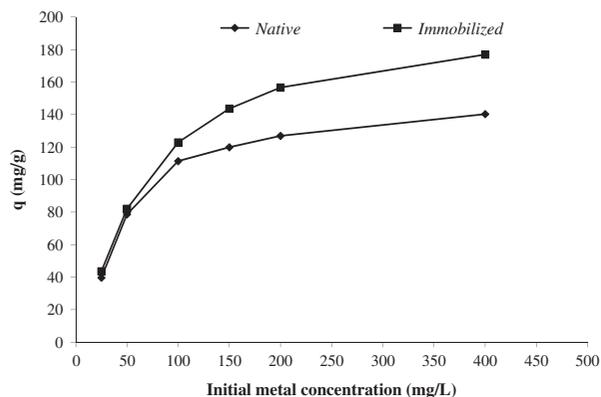


Fig. 4. Effect of initial metal concentration on uptake of Cu (II) by *M. spicata* distillation waste biomass.

information about comparison among different biomaterials under different operational conditions, designing, and operating procedures [29,30]. Langmuir and Freundlich equations were applied for fitting the data in order to examine the relationship between amount of sorbed metal (q_e) and aqueous solution concentration (C_e) at equilibrium. The Langmuir parameters were determined from a linearized form of Eq. (3), represented by:

$$C_e/q_e = 1/q_{\max}K_L + C_e/q_{\max} \quad (3)$$

where q_e is the metal ion sorbed (mg/g), C_e is the equilibrium concentration of metal ion solution, and K_L is the Langmuir adsorption constant. Adsorption-partition constants were determined for Cu(II) using the following log form of the Freundlich isotherm equation (4):

$$\log q_e = 1/n \log C_e + \log k \quad (4)$$

where k and n are Freundlich constants, q_e is metal ion sorbed (mg/g), C_e is the equilibrium concentration of metal ion solution (mg/L). The constant k was

determined by linear regression from the plot of $\log q_e$ against $\log C_e$ [31].

Only correlation coefficient (R^2) cannot be relied on solely to assess the goodness of fit [30–32]. The Langmuir equation better represented the experimental isotherm data due to the high value of the correlation coefficient (R^2) and close agreement of the experimental and calculated values (Table 1).

3.5. Effect of time

The results obtained showed that contact time of 180 min was necessary to reach the equilibrium in Cu (II) uptake (Fig. 5). It is known that rate of metal uptake is influenced by factors affecting mass transfer from bulk solution to binding sites. From the results obtained, the metal uptake was increased with the increase in time contact. Two different kinetic models Lagergren pseudo-first-order model and pseudo-second-order model were used to adjust the experimental data of Cu(II) biosorption on to native and alginated *M. spicata* distillation waste biomass. A comparison between the two kinetic models is given in Table 2 for native and alginated waste biomass, respectively, which shows that Cu(II) uptake by both native and

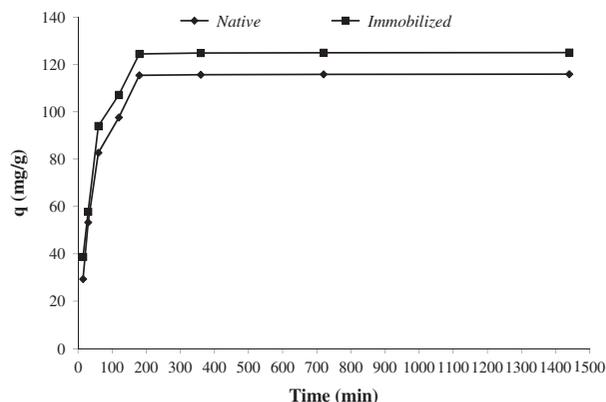


Fig. 5. Effect of time on the uptake of Cu(II) by *M. spicata* distillation waste biomass.

Table 1

A comparison between Langmuir and Freundlich isotherm parameters on the uptake of Cu(II) by *M. spicata* distillation waste biomass

Biomass	Langmuir isotherm parameters			Experimental value q (mg/g)	Freundlich isotherm parameters		
	q_{\max} (mg/g)	K_L (1/mg)	R^2		K (mg/g)	R^2	$1/n$
Native	144.93	0.670	0.9989	140.30	32.08	0.8360	0.2811
Immobilized	185.19	0.591	0.9982	176.96	35.29	0.9249	0.3072

Table 2

A comparison between pseudo-first-order and pseudo-second-order kinetic models for Cu(II) uptake by *M. spicata* distillation waste biomass

Biomass	Pseudo-first-order kinetic model			Experimental value q_e (mg/g)	Pseudo-second-order kinetic model		
	q_e (mg/g)	$K_{1,ads}$ /(min)	R^2		q_e (mg/g)	$K_{2,ads}$ (g/mg/min)	R^2
Native	96.36	1.5×10^{-2}	0.9615	115.86	131.57	2.36×10^{-4}	0.9942
Immobilized	98.78	1.5×10^{-2}	0.9457	124.98	138.88	2.08×10^{-4}	0.9960

alginate *M. spicata* distillation waste biomass followed the pseudo-second-order kinetics rather than pseudo-first-order kinetics [21–23,33]. In the case of wastewater treatment process, the equilibrium time is one of the most important parameters [34].

Modeling of the data was performed by using Lagergren pseudo-first-order model and pseudo-second-order model. Pseudo-first-order equation (5) is expressed as:

$$\log(q_e - q) = \log q_e - (K_{1,ads}t) / 2.303 \quad (5)$$

Pseudo-second-order equation (6) is given as:

$$t/q = 1/K_{2,ads} q_e^2 + t/q_t \quad (6)$$

where q_t is the adsorbed metal ions (mg/g) at time t (min), $K_{1,ads}$ is the first-order reaction of adsorption/(min), $K_{2,ads}$ the pseudo-second-order rate constant of adsorption mg/g/(min), q_e , the mass of metal [25]. Careful evaluation of results suggested that uptake process followed pseudo-second-order rather than pseudo-first-order [30]. The pseudo-second-order kinetic model generally presents a better rational prediction as it showed high correlation coefficients in current case (Table 2). The calculated sorption capacity values resulted from second-order kinetic model were in a good fit with the experimental sorption capacity values.

3.6. Effect of pretreatment

The effect of pretreatment on uptake capacity (mg/g) of native and alginate *M. spicata* distillation waste biomass is shown in Fig. 6. Physically treated native *M. spicata* distillation waste biomass showed metal sorption capacity (mg/g) in the following order: Boiled (118.26) > Heated (117.76). The metal sorption capacity (mg/g) of base treated native *M. spicata* distillation waste biomass was: NaOH (138.44) > Ca(OH)₂ (133.1). There was a maximum increase in the sorption

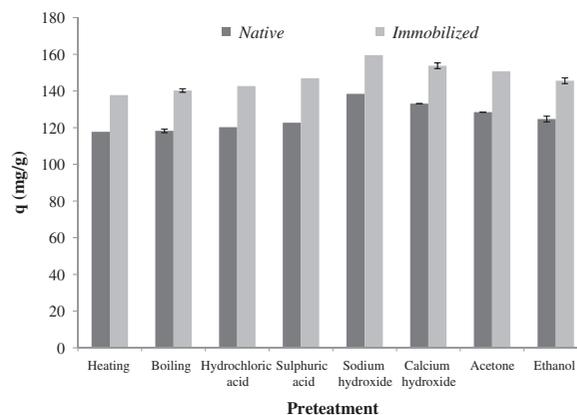


Fig. 6. Effect of different pretreatments on the uptake of Cu(II) by *M. spicata* distillation waste biomass.

capacity of biosorbent after basic treatment. After acidic treatment, the biosorption capacity (mg/g) was: H₂SO₄ (122.7) > HCl (120.26). The effect of other chemical pretreatments on biosorption capacity (mg/g) of native *M. spicata* distillation waste biomass was as follows: Acetone (128.48) > Ethanol (124.7).

For alginate biomass, the effect of various treatments on its uptake capacity (mg/g) was found to be as follows: basic treatment (NaOH (159.54) > Ca(OH)₂ (153.76)), acidic pretreatment (H₂SO₄ (146.92) > HCl (142.70)), organic pretreatment (acetone (150.70) > Ethanol (145.58)), physical pretreatment (Boiled (140.26) > Heated (137.76)). Physical pretreatment of waste biomass was done to check the uptake of Cu(II) after boiling and heating. Biosorption of Cu(II) was increased after boiling and heating. It may be due to the introduction of more sorption sites on biomass surface. There was a significant increase in the metal sorption capacity due to the base pretreatment because of the destruction of cellulose polymer. Removal of surface impurities, rupture of cell membrane and exposure of available binding sites for Cu(II) after pretreatment may be the reason for the increase in metal biosorption after alkali pretreatment of the biomass.

After acidic pretreatment, the biosorption capacity of *M. spicata* distillation waste biomass was in following order: $\text{H}_2\text{SO}_4 > \text{HCl}$. *M. spicata* waste distillation biomass pretreatment by acetone resulted in improved metal uptake capacity. Ethanol pretreatment of the biomass results in the esterification of the carboxylic acids present on the cell wall of the biosorbent which may cause the decrease in the uptake of metal [35].

3.7. Desorption

Desorption of loaded native and alginate *M. spicata* distillation waste biomass with different acids (0.1 N) at a pH of 5.0 and 30°C is given in Fig. 7. The percentage recovery of Cu(II) from native and alginate *M. spicata* distillation waste biomass (mg/g) was in the following order: $\text{NaOH} > \text{HCl} > \text{EDTA}$. The data showed that more than 90% Cu(II) was desorbed from native and alginate *M. spicata* distillation waste biomass by NaOH.

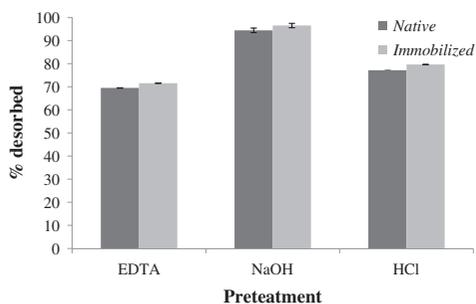


Fig. 7. Effect of desorption on the loaded waste biomass.

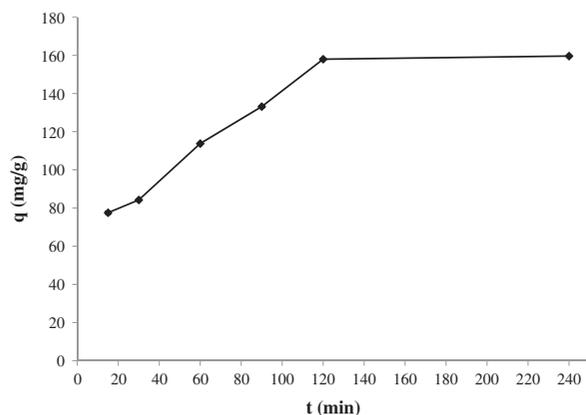


Fig. 8. Effect of time on the column study of uptake of Cu(II) by immobilized *M. spicata* distillation waste biomass.

3.8. Column study

The column study was performed by fixing the initial concentration of solution at 100 mg/L, pH 5.0, 30°C temperature, and biosorbent dose of 0.05 g/100 mL with a flow rate of 4 mL/min for a time range of 360 min. The results are shown in Fig. 8. The rapid Cu(II) removal was observed in first 30 min. Contact time of 120 min was sufficient to achieve metal sorption equilibrium. The best fit for the experimental data was achieved by the application of pseudo-second-order kinetic equation. In order to investigate the mechanism of biosorption, kinetic models have been applied to test the experimental data. The kinetics data fitted well to pseudo-second-order models. The experimental uptake capacity of *M. spicata* distillation waste biomass was more in the batch experiments than in column setup [36]. Kinetic modeling successfully replaces time and material consuming experiments, and can be used to find important parameters for bioreactor design.

3.9. FTIR analysis

The FTIR analyses were conducted to identify characteristic functional groups and their possible interactions with metal ions (Fig. 9(a)–(c)). The absorption peaks at 3,580–3,650 cm^{-1} were due to the presence of $-\text{OH}$ group which indicated presence of alcoholic and phenolic functional groups on biomass surface. Peaks appearing between 3,300 and 3,500 cm^{-1} were due to NH_2 scissoring (1° -amines) and NH_2 , N–H wagging vibrations and confirmed the presence of amine in biomass cells. The absorption peaks also appeared near 2,930 cm^{-1} ($-\text{CH}_3$ groups), 2,350 cm^{-1} ($-\text{C}\equiv\text{N}$ groups), and 1,600–1,800 cm^{-1} ($\text{C}=\text{O}$ groups). The decrease in absorption peak intensity as well as disappearance of some peaks indicates that COO , $-\text{CH}_3$, $-\text{OH}$, and $-\text{C}\equiv\text{N}$ groups were involved in biosorption process. A new peak at 1,735 cm^{-1} corresponded to the $-\text{C}=\text{O}$ groups, suggesting that $-\text{C}-\text{O}$ groups oxidized to $\text{C}=\text{O}$ groups during biosorption process (Fig. 9(c)). The significant changes in the vibrational frequencies implicated that carboxylic, carbonyl, and nitrile groups played vital roles during biosorption process and interacted with Cu(II) ions through ion exchange and complexation reactions. The other groups involved in the metal uptake process may be alcoholic and phenolic [8–37].

3.10. Statistical analysis

Tukey's HSD (Honest Significant Difference) test is a post hoc test performed after an analysis of variance

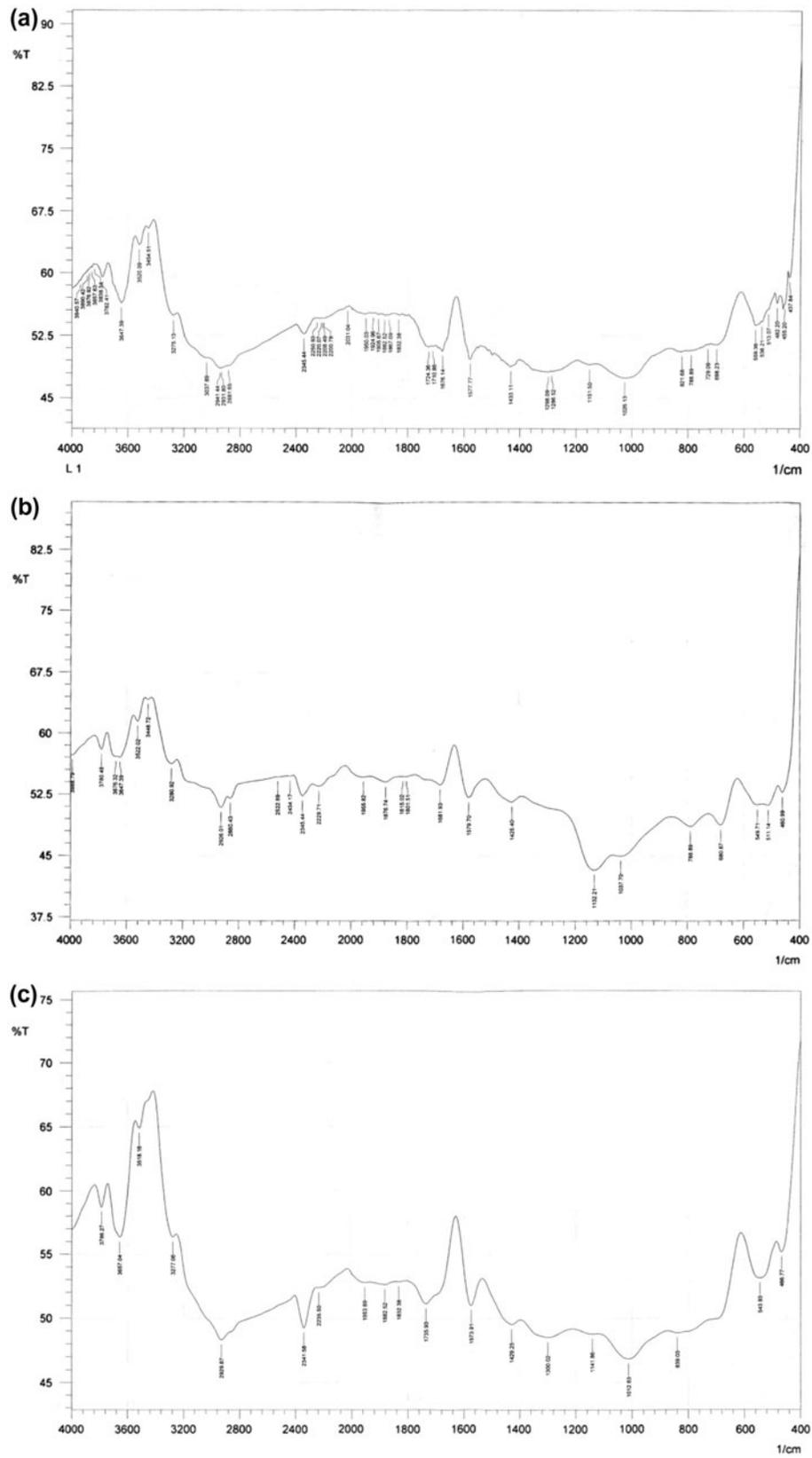


Fig. 9. FTIR spectra of *M. spicata* distillation waste biomass (a) native, (b) immobilized, and (c) Cu(II) load immobilized.

Table 3
Tukey's HSD for Cu(II) uptake by *M. spicata* distillation waste biomass at optimized conditions

Contact time	diff.	lwr.	upr.	<i>p</i> adj.
30–15	19.100	18.674	19.526	0.000
60–15	55.280	54.854	55.706	0.000
120–15	68.440	68.014	68.866	0.000
180–15	85.720	85.294	86.146	0.000
360–15	86.120	85.694	86.546	0.000
720–15	86.220	85.794	86.646	0.000
1,440–15	86.300	85.874	86.726	0.000
60–30	36.180	35.754	36.606	0.000
120–30	49.340	48.914	49.766	0.000
180–30	66.620	66.194	67.046	0.000
360–30	67.020	66.594	67.446	0.000
720–30	67.120	66.694	67.546	0.000
1,440–30	67.200	66.774	67.626	0.000
120–60	13.160	12.734	13.586	0.000
180–60	30.440	30.014	30.866	0.000
360–60	30.840	30.414	31.266	0.000
720–60	30.940	30.514	31.366	0.000
1,440–60	31.020	30.594	31.446	0.000
180–120	17.280	16.854	17.706	0.000
360–120	17.680	17.254	18.106	0.000
720–120	17.780	17.354	18.206	0.000
1,440–120	17.860	17.434	18.286	0.000
360–180	0.400	-0.026	0.826	0.074
720–180	0.500	0.074	0.926	0.016
1,440–180	0.580	0.154	1.006	0.005
720–360	0.100	-0.326	0.526	0.990
1,440–360	0.180	-0.246	0.606	0.816
1,440–720	0.080	-0.346	0.506	0.997

Note: The Tukey HSD critical value is 4.8962205.

(ANOVA) test. The purpose of Tukey's HSD test is to determine which groups in the sample differ as ANOVA cannot tell the researcher which groups differ. Tukey's HSD can clarify to the researcher which groups among the sample in specific have significant differences. HSD represents the minimum distance between two group means that must exist before the difference between the two groups is to be considered statistically significant. Tukey HSD for Cu(II) uptake by *M. spicata* distillation waste biomass at optimized conditions was performed (Table 3). The Tukey HSD critical value was 4.8962205. All the data groups having difference more than Tukey HSD critical value 4.8962205 were found significant.

4. Conclusions

M. spicata distillation waste biomass was effectively and efficiently used for Cu(II) removal in the present study. Langmuir adsorption isotherm and

pseudo-second-order kinetic model fitted well to experimental data of native and alginate *M. spicata* distillation waste biomass. The desorption ability of different desorbing agents used in the present study was in following order: NaOH > EDTA > HCl. FTIR analysis demonstrated the involvement of carboxylic, carbonyl, nitrile, alcoholic, and phenolic groups in metal uptake process.

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