

Potential application of *Combretum indicum* biomass for the efficient biosorption of Ni(II) and Cu(II) from aqueous medium

Anum Tahir^{a,b}, Muhammad Salman^{a,*}

^aCentre for Applied Chemistry, School of Chemistry, University of the Punjab, Lahore-54590, Pakistan, email: anumtahir@ucp.edu.pk (A. Tahir)

^bFaculty of Sciences, University of Central Punjab, Lahore-54000, Pakistan, email: salman.chem@pu.edu.pk (M. Salman)

Received 3 March 2022; Accepted 29 July 2022

ABSTRACT

The target of this research was to scrutinize a creeper plant, that is, *Combretum indicum* as a novel, eco-friendly, easily attainable and low cost biosorbent for the targeted metal ions' removal. Ni(II) and Cu(II) ions were withdrawn from their aqueous solution by using the biosorbent. The said biomass was studied and characterized in detail via multiple analyzing techniques including scanning electron microscopy-energy-dispersive X-ray analysis, thermogravimetry, Brunauer–Emmett–Teller surface analysis and Fourier-transform infrared spectroscopy. After the thorough analysis the optimum dosage of C.I. was found to be 0.5 g for both adsorbates. The optimum time of contact for C.I. was 25 min for Cu(II) and 30 min for Ni(II) metal ions. Optimum pH was found to be acidic. The maximum adsorption capacities for Ni(II) and Cu(II) were found to be 27.8 and 12.1 mg/g, respectively. Equilibrium modeling revealed that experimental data fits best in Freundlich's isotherm for both metals. The thermodynamic research depicted the process as spontaneously occurring and endothermic. The biosorption of the metal ions was in accordance with the pseudo-second-order kinetic model.

Keywords: Nickel(II); Copper(II); Adsorption; *Combretum indicum*; Kinetics; Isotherm; Thermodynamic

1. Introduction

Our world today is a much better place to live in because of the technological advancements and the developments mankind has made worldwide. Unfortunately, this betterment of the globe is coming at a big cost, that is, ever increasing pollution and water contamination. Several industrial actions happening around the world are the main reasons for the contamination of water, water bodies and sediments etc. [1,2]. These increasing amounts of the contaminants have exceeded the set limits by Environmental Protection Agency and World Health Organization. Mostly these pollutants are of non-biodegradable origin metal ions [3]. These metal ions especially nickel and copper are at

the list's top among the pollutants that have contributed in global pollution [4]. The amount of these compounds should be lessened to deal any increasing legislative standards. These hazardous chemicals not only affect the microorganisms but also the humans especially the brain and body's nervous system [5,6].

Nowadays many physiochemical methodologies are employed for the reduction of heavy metals from water bodies [7]. These includes membrane separation, chemical precipitation, photocatalysis and sorption etc. [8].

Although the above-mentioned approaches are efficient but these also offer many drawbacks for example excessive use of chemicals, increase cost and generation of toxic sediments [9]. The biosorption approach is the

* Corresponding author.

metal removal by the bio-origin substances [10–12]. This method, by utilizing agricultural waste and biological naturally occurring substances, removes the metal contaminants from water [7,13–15]. Agricultural by products used as bio sorbents serve as an ecological friendly approach for removing the waste [16].

Nickel and copper have extreme toxicity even if present in trace amounts [17,18]. These metal ions are a source of various health concerns including cardio-vascular diseases, intestinal and gastro infections, lethargy, cancer, diabetes, brain malfunctioning and liver and kidney disorders [19–21]. This study will test the use of novel biosorbent, *Combretum indicum* also known as *Quisqualis indica* and Rangoon creeper, for the very first time for the removal of copper and nickel ions. The sorption and kinetic studies of the Rangoon creeper plant for removal of these ions were studied and batch tests were applied.

The experimental results shows that the plant under study can efficiently be used for the removal of the targeted metal ions and also further pollutants from our environmental on the larger scale as in various industries. This work done could prove as an excellent source for wastewater treatment and will serve as a good addition in the bio-materials used for water purification as in its present raw form (C.I.) and also in its modified form where the biosorbent will be activated by some foreign chemicals. The targeted study achieved desired results, first regarding the optimum parameters for the efficient removal of said metal ions by *Combretum indicum*. Secondly the sorption and kinetic studies were successfully examined to find out the rate and progress of the reaction.

2. Materials and methods

2.1. Preparation of the biosorbent

In this proposal the *Combretum indicum* was used as a plant biosorbent, targeting nickel and copper metal ions. The plant (whole biomass) was collected from different areas of Lahore as it is easily grown as an ornamental plant and is widely available. Following the direct drying in sun, the plant was first thoroughly cleaned with the distilled water and dried in the oven at 70°C for 6 h. The dried mass was then grinded to a fine powder by using Biomass Hammer Mill Grinder (Model no: SG65×55) and then it was passed through 80-mesh sieve. The powder was washed with deionized water multiple times until the color of the plant stopped leaching out [22]. Afterwards the biomass was dried in oven at temperature range of 65°C–70°C (until the powder completely dried). The dried biomass was stored in a dry place for further use.

2.2. Characterization of biosorbent

For analyzing the functional groups present on *Combretum indicum* multiple analysis were performed utilizing Fourier-transform infrared (FTIR) spectrophotometer by KBr disc method (Perkin Elmer Spectrum RX1, Massachusetts, United States). The biomass was analyzed via FTIR both before and after the biosorption of the targeted copper and nickel metal ions. To study the morphology of the plant

adsorbent and the morphological changes happened upon the metal sorption, the loaded and unloaded plant material was subjected to scanning electron microscopy (SEM) analysis accompanied with the energy-dispersive X-ray analysis (EDX). SEM-EDX (SEM JSM-IT100) combined gave a better insight into not only the plant morphology but also about the elemental constitution of the material under study [23].

The biosorbent (both loaded and unloaded) was analyzed also by thermogravimetry (TGA-SDT Q600), for a better understanding towards the plant thermal properties and its compositional degradation [24]. To comprehend the specific surface area and also the adsorptive power (physisorption) of *Combretum indicum*, it was characterized by Brunauer–Emmett–Teller (BET) surface area analyzer (NOVA 2200e Make by Quantachrome, USA) [25]. The crystalline composition of the said adsorbent was studied by the analysis done by X-ray diffraction analysis utilizing JDX-3532, JEOL (Japan) XRD analyzer [26].

2.3. Preparation of the metal ions' solutions (sorbate)

Ni(II) and Cu(II) stock solutions of 1,000 ppm were prepared with the deionized water by using analytical grade (Merck, Germany) nickel nitrate and copper nitrate respectively. Testing standards of various concentrations were prepared by diluting the original stock solutions of nickel and copper.

2.4. Apparatus and analysis technique

Ni(II) and Cu(II) solutions were analyzed by atomic absorption spectrophotometer (Perkin Elmer AAnalyst 100) at 232.0 and 324.8 nm, respectively.

Batch experiments were carried out in the conical flasks of 250 mL by shaking them on the orbital shaker (VORTEX Model No: OSM-747). The solutions' pH was adjusted by using 0.1 M NaOH and 0.1 M HCl solutions with the assistance of digital pH meter (ADWA, 130).

2.5. Batch biosorption experiments

Multiple experiments were performed using the 50 ppm of the nickel and copper solutions. The effects of different parameters were studied, that is, adsorbent dose, temperature, pH, contact duration, initial metal ion concentration for the uptake of heavy metal from their respective solutions by adsorption. Effect of change of one parameter was observed keeping all other constant and then calculated the optimized condition of that parameter at which its absorption capacity was optimum. Optimized conditions for absorption of Ni and Cu were checked by changing the measurement criteria such as pH value ranging from (1–8), time of contact of metal and adsorbent (5–45 min), range of the set temperature (10°C–70°C) and concentration of metal ions initially were ranged between (20–180 ppm). For the evaluation of the concentration of Ni and Cu in the solution, filtration was carried out of the processed solutions first and then the resultants were analyzed by subjecting the samples to flame atomic absorption spectrophotometer. The obtained results were then quantified against standard solutions of their respective metal ions. The sorption capacity of metal ions was calculated using formula:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

where ' m (mg)' is the dose of the plant adsorbent, q_e (mg/g) indicates the biosorbent uptake capacity, C_0 (mg/L) is the starting initial concentration and C_e (mg/L) is the concentration at equilibrium of the metal ions and ' V (mL)' is the volume of solution studied.

2.6. Equilibrium study

Working solutions of Ni(II) and Cu(II) of varying concentrations ranging from (20, 40, 60 to 180 ppm) were prepared. Aliquot (50 mL) of each was taken and subject to adsorption under the optimum conditions gained from process parameter study of the concerned metal ions. Famous equilibrium models including Freundlich model and Langmuir model were employed on the gained results to evaluate the equilibrium data and their optimum parameters were computed from respective plots [27]. For linear and nonlinear plotting Microsoft Excel 2013 software was used. All experiments were carried out thrice and the mean of the resultant values are reported. Root mean square error (RMSE) and regression analysis (R^2) have been calculated to study the error of predicted models and the stability of mathematical models. RMSE is calculated by dividing the sum of squares of difference between experimental data $q_{e(\text{exp})}$ and model predicted $q_{e(\text{cal})}$ for metal adsorption to number of data points (N) then square root of this obtained data was taken.

$$\text{RMSE} = \frac{\sqrt{\sum (q_{e(\text{cal})} - q_{e(\text{exp})})^2}}{N} \quad (2)$$

3. Results and discussion

3.1. Surface analysis by SEM

Bulk density of the biosorbent was 0.15 g/cm³. The changes in the surface morphology of the biosorbent can be easily detected by using SEM, as this method gives qualitative knowledge of the structure of the surface [28].

Fig. 1a represents the morphology of the biomass surface and Fig. 1b and c explain the Ni(II) and Cu(II) loaded biomass. The difference in surface roughness in the concerned figures affirms the attachment of the metal ion to the biosorbent surface [29].

3.2. Inspection by FTIR

Also, the metal loaded and unloaded plant biosorbent *Combretum indicum* was subjected to FTIR analysis. FTIR spectra obtained gave the information regarding the multiple functional groups present in the plants that may be responsible for binding the metal ions to the plant. FTIR analysis of the raw biosorbent and of the Cu(II) loaded and Ni(II) loaded is shown in Fig. 2. The broad peak appeared at 3,287.34 cm⁻¹ indicated the presence of hydroxyl group. A sharp peak appeared 1,745.28 cm⁻¹ indicated the presence

of carbonyl group and peaks appeared at 1,228.14; 1,188.47 and 1,021.09 cm⁻¹ indicated the presence of carboxyl group on the surface of biosorbent. All the said functional group contain electronegative oxygen that may responsible for metal attachment to the biosorbent surface.

3.3. Biosorbent analysis by thermogravimetry

A very important and vital analytical analysis that is globally carried out to investigate the thermal aspects of many carbonaceous plant materials is thermogravimetric analysis [30]. The results obtained from TGA give us thorough knowledge of the changes happening in the natural materials with the changing temperatures and how well a material can work under variety of thermal conditions [31]. The information obtained can guide us about the thermal stability and degradation of the subjected samples. *Combretum indicum* was analyzed to check the thermal endurance by using TGA for the varying temperatures ranging from 27°C to 900°C. Nickel and copper loaded plant-sorbents were also subjected to thermogravimetric analysis (Fig. 3). TGA results obtained the usual reported mass loss of the biosorbent in three stages.

- The first degradation of the plant material was observed below 200°C, which may indicate the removal of water molecules adhered physically to the *Combretum indicum*. The loss in the overall mass of the plant may also have occurred due to the degradation of the volatile substances that were present in the taken plant sample, for temperature up to 200°C.
- The next degrading pattern observed around the temperature of 400°C, which was maybe due to the break down and decomposition of the hemi cellulosic and cellulosic constituents of the plant anatomy along with the lignin present.
- The further mass decomposition in the third stage was due to the degradation of the carbonaceous matter left in the plant structure. This was observed around the temperature of 500°C and above [32].
- The increased thermal endurance and degradation observed at relatively higher temperatures was seen in the results of metal loaded biosorbent, indicating the metal adhered to the plant [33].

3.4. Analysis by EDX

Combretum indicum was subjected to EDX analysis both before and after the metal attachment. The analyzed results displayed the addition of targeted Ni(II) and Cu(II) on the plant. The mapping of EDX is shown in the diagram. Fig. 4a displays the peaks given by the plant before it adsorbed metal ions, showing that the calcium, copper, oxygen and carbon are the main constituents of C.I. Whereas upon interaction with metal the result indicates the incorporation of Cu(II) (Fig. 4b) and Ni(II) (Fig. 4c). This affirms the efficient attachment of the targeted metal ions with the active sites present in C.I. and ensures that the biomass could be efficiently used for the removal of the respective metal ions.

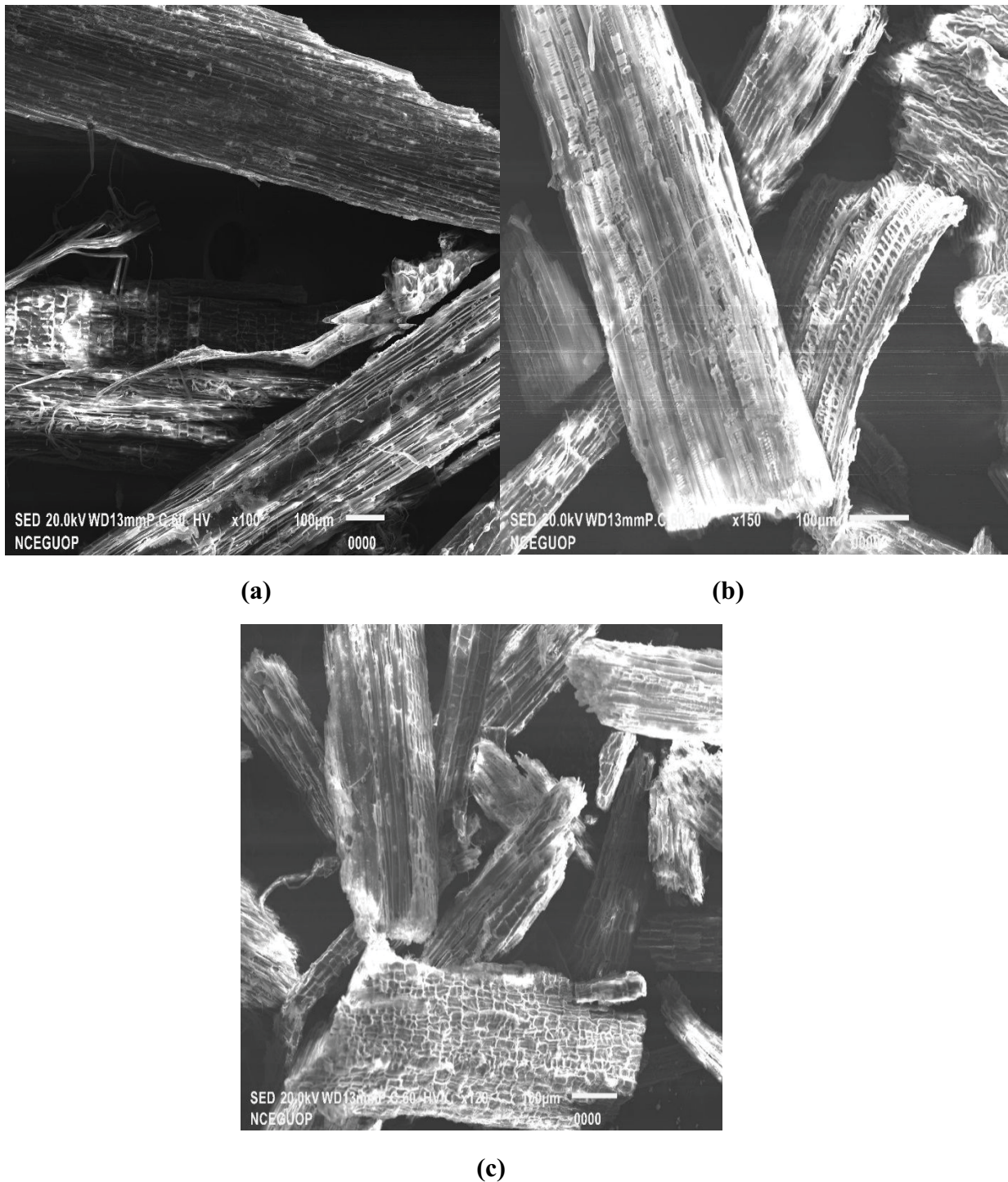


Fig. 1. SEM image of *Combretum indicum* (unloaded) at $\times 100\mu\text{m}$ magnification, Cu-loaded biosorbent at $\times 100\mu\text{m}$ magnification, Ni-loaded biosorbent at $\times 100\mu\text{m}$ magnification.

3.5. Brunauer–Emmett–Teller surface area analyzer

The adsorption done by a plant material is a complex procedure done in multiple, gradual steps. That's why there are variety of aspects that affect the uptake of the sorbates by the sorbents, one of the very important aspect is the size of the sorbent pores [34]. The general reported sizes of the pores

are macropores, mesopores and micropores with diameters ranging from >50 to <2 nm, respectively [35]. By looking into the surface chemistry of the *Combretum indicum* by the BET analyzer we can easily understand the adsorption of nickel and copper ions [32].

As per the results, *Combretum indicum* showed promising results as it was found to have a prominent and vast

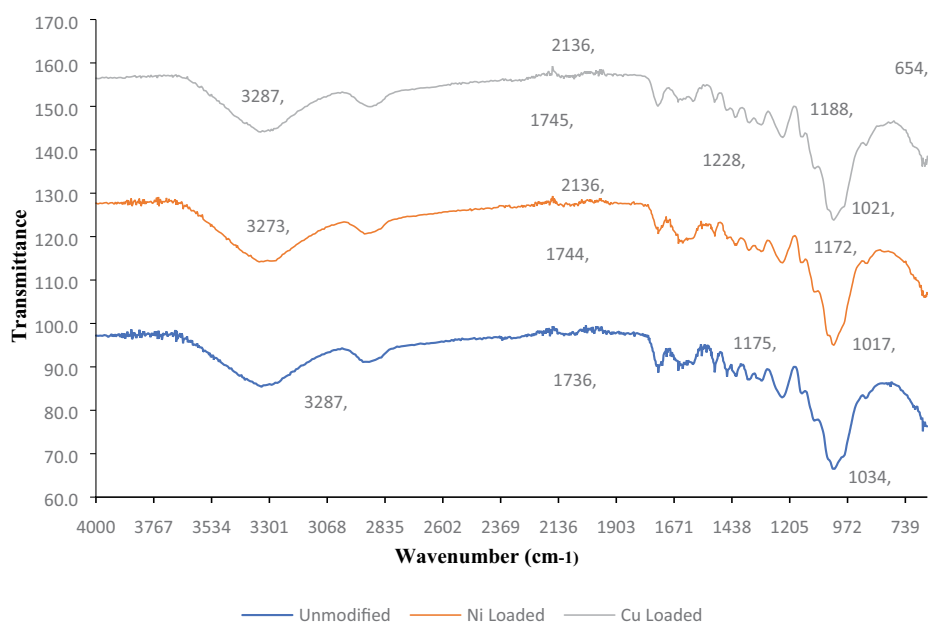


Fig. 2. FTIR spectra of unloaded and metal loaded biosorbent.

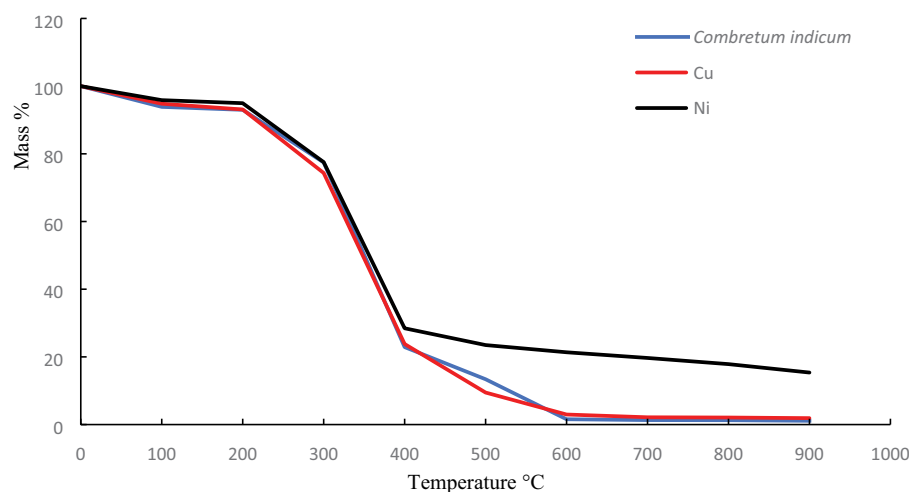


Fig. 3. TGA analysis of unloaded and metal loaded C.I.

surface area and wide pore size arrangement. The BET surface area of the analyzed plant adsorbent is $51.438 \text{ m}^2/\text{g}$. also for *Combretum indicum* the single point average pore volume of pores in total was $14.9558 \text{ cm}^3/\text{g}$ (Table 1). The obtained data was very desirable for the removal of the metal ions from their solution medium with the help of adsorption process.

3.6. Effect of adsorbent dose

The uptake of the metal ions from their respective solutions with the change in the adsorption dose was studied with the help of multiple experiments done in series.

The gathered results are displayed in Fig. 5a (removal of nickel) and 5b (removal of Cu). As shown in the figure it can clearly be seen that the uptake capacity of the adsorbent has raised with the increase in its concentration. This increasing trend of the sorption starting to decrease once after the saturation point. The initial increase in adsorption with increasing dose depicts the availability of more active binding sites in the biomass for the metal ions attachment. However, after the specific value of biomass the adsorption started to decrease, showing the aggregation or the coagulation of the plant biomass, resulting in the less available active sites for the metal ions [28]. This step makes it clear that, what is the trend of the quantitative binding

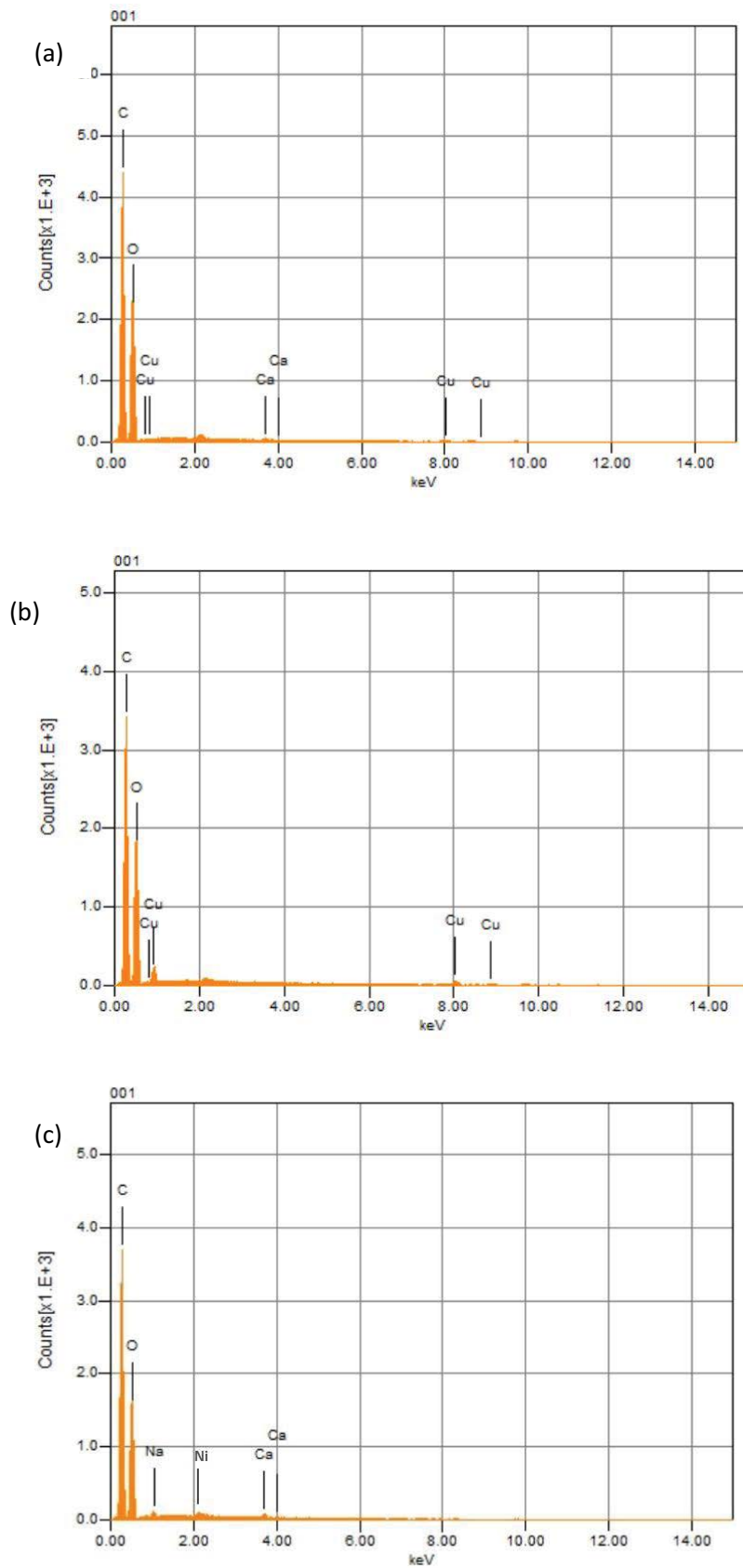


Fig. 4. (a) EDX of unloaded C.I., (b) EDX of Cu(II) loaded C.I., and (c) EDX of Ni(II) loaded C.I.

Table 1
Surface properties of *Combretum indicum*

Surface properties	Values
BET surface area	51.438 m ² /g
Single point average pore volume	14.9558 cm ³ /g
Cross section	16.200 Å ²

capacity of the said biomass for the both targeted metals. The trend was found different for both Ni(II) and Cu(II) ions. The optimum adsorbent dose was taken as 0.5 g for both the metals respectively.

When the adsorbent was present in low concentration, the ratio of metal ions uptake and the available binding

sites was high. So, all the targeted Ni(II) and Cu(II) ions were attached to the binding area of the adsorbent [27]. This ratio started to decrease when the adsorbent concentration increased, this decrease in the ratio is due to the less metal ions' attachment as most of the active sites are already occupied [18].

3.7. Adsorption of metal ions as a function of contact time

This process parameter is very important to gain knowledge regarding the optimum time that is necessary for the removal of heavy metal ions. It has been discussed in different researches that adsorption process happens in dual/bi phases [36]. During the first step, a rapid continuous increase in the capacity of the biosorbent is observed. This may be observed due to excessive

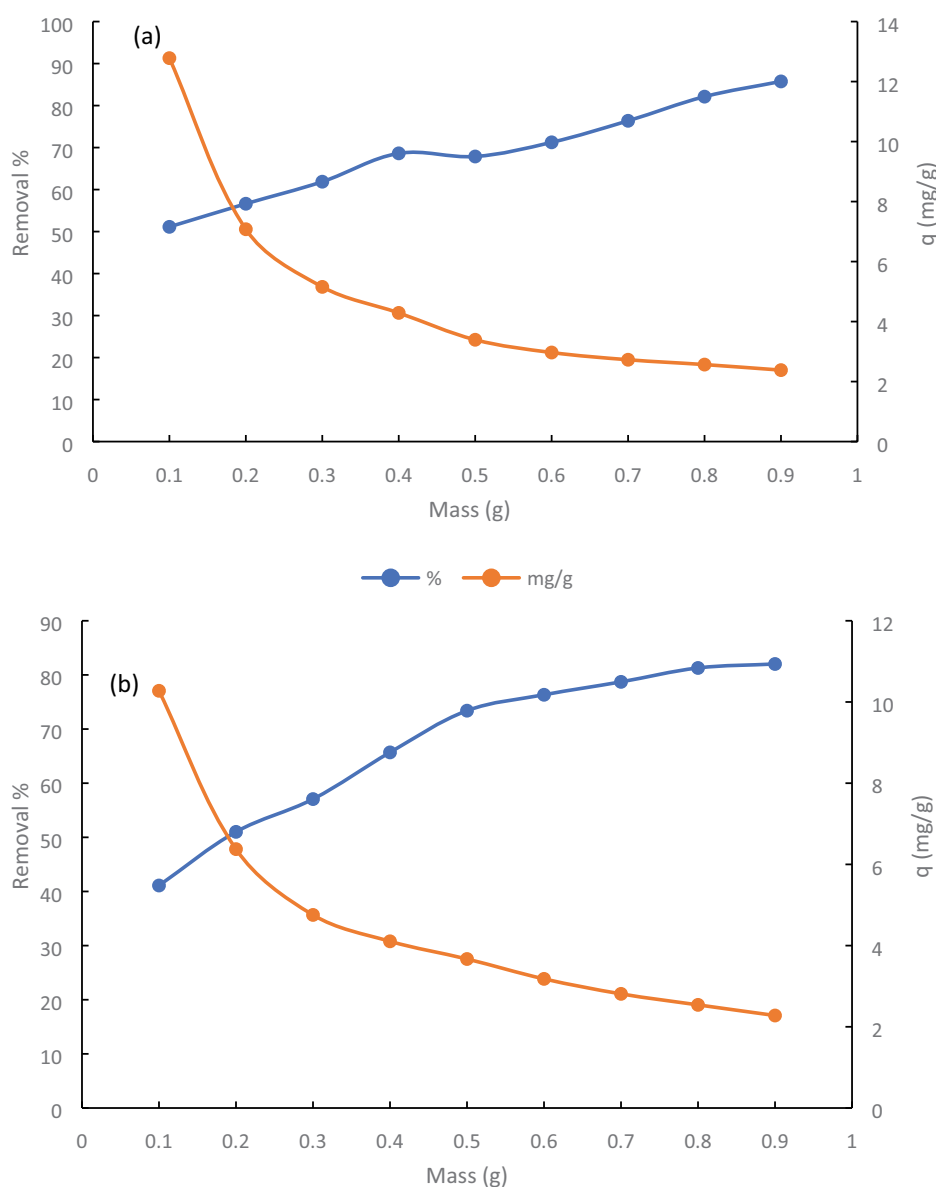


Fig. 5. Effect of adsorbent dose on removal of (a) Ni(II) and (b) Cu(II).

binding sites available initially at the surface of biosorbent. While in second phase the adsorption has been observed in a decreasing pattern because the initial unoccupied sites at surface were accumulated by the metal ions. The same pattern was observed for both the metals taken. The optimum time was found to be 25–30 min in both the cases. The maximum time of equilibrium achieved at 25 and 30 min with a maximum adsorption capacity of 3.67 and 3.46 mg/g for Ni(II) and Cu(II) respectively (Fig. 6a and b).

3.8. pH profile

The metal uptake capacity of the biosorbent is affected by the pH of solution. The degree of ionization, nature of the metal ions and the adsorbent charge can easily be explained by studying the change in pH [37]. Number of unsaturated active sites of the plant biomass are widely affected by pH variation. Series of experiments were

performed by changing the pH of the working solution within the range of 1–10 by keeping the other factors constant. The optimum value at which the adsorbent showed the maximum activity is acidic, that is, pH-5 as shown in Fig. 7a and b. Increase in the pH resulted in increase of the percentage removal of the metal ions, this happened due to the removal of protons from the binding sites of the biosorbent. This deprotonation with varying pH resulted in the more available sites for the metal ions to adhere with the biomass. It was also observed that after a specific limit the adsorbent metal uptake decreased due to the metal-OH formation which resulted in the precipitation of the metal ions. The maximum efficiency is shown by the biosorbents generally at slightly acidic pH [38].

While at the high acidic pH the cations were repelled by the already saturated protonated areas in the biomass. This similar behavior is observed for other various biosorbents [39,40].

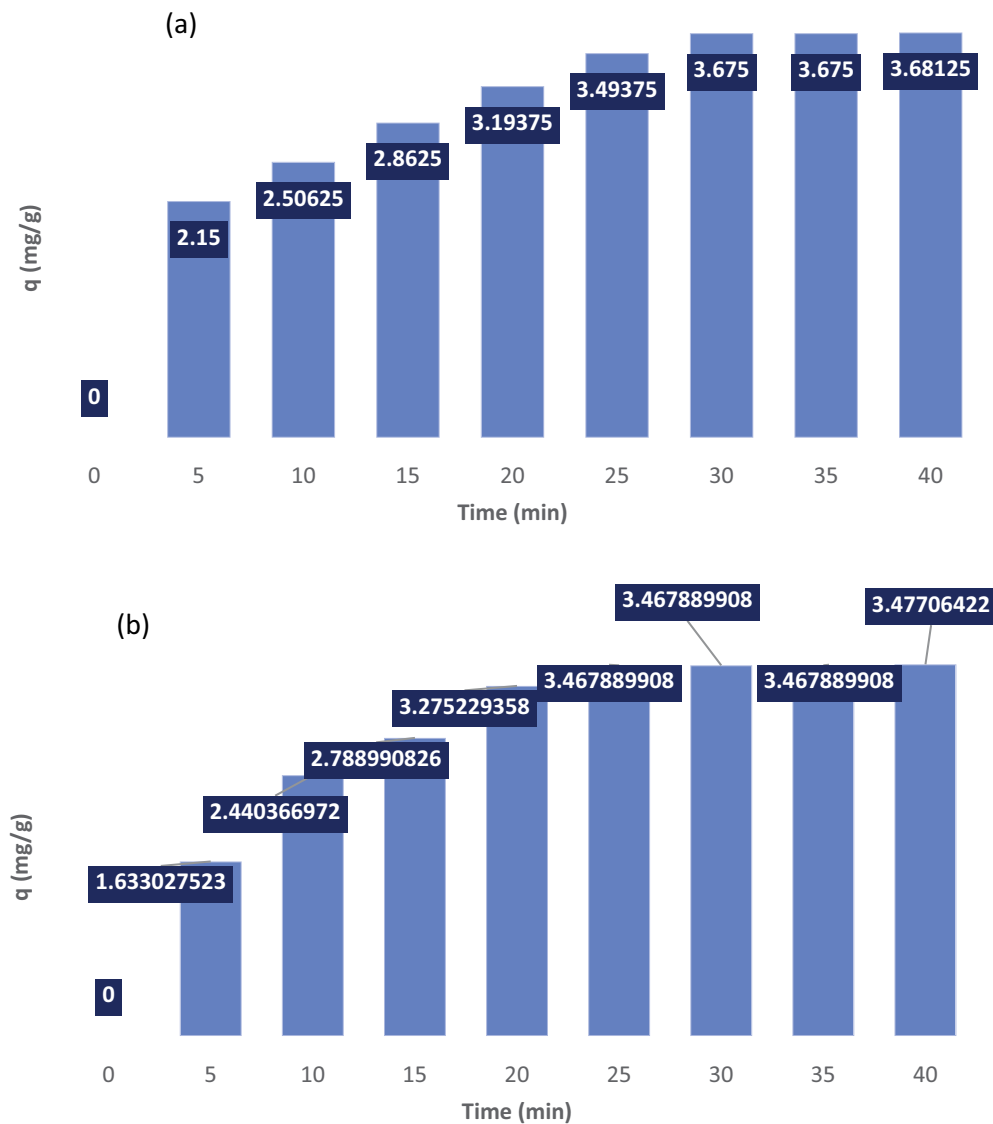


Fig. 6. Effect of time on adsorption of (a) Ni(II) and (b) Cu(II).

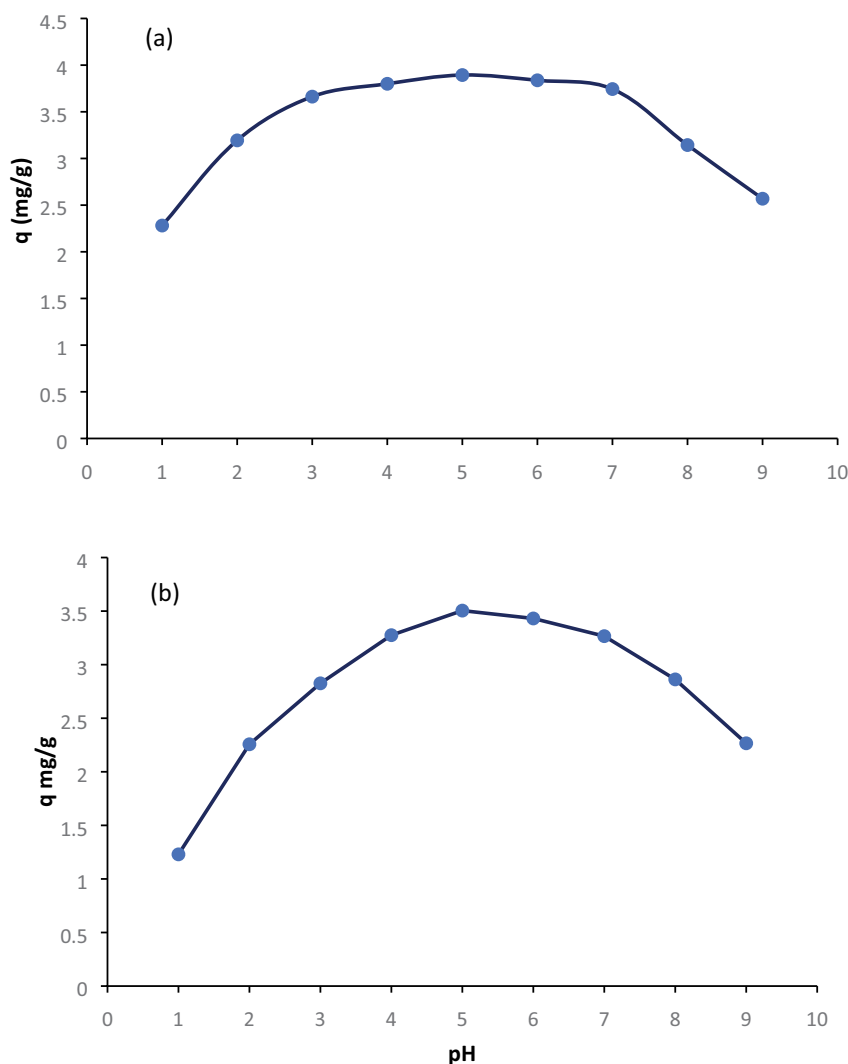


Fig. 7. Effect of pH on adsorption of (a) Ni(II) and (b) Cu(II).

3.9. Adsorption kinetics

Optimum time for maximum adsorption of metal by our biomass by keeping all the other factors constant is studied and explained in Fig. 8a and b:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e (mg/g) and q_t (mg/g) is the metal uptake capability of plant adsorbent at equilibrium and instantaneous time t , respectively. k_1 (min^{-1}) and k_2 (g/mg/min) are the constants of pseudo-first-order reaction and pseudo-second-order reactions respectively. According to pseudo-first-order, biosorption rate is directly related to number of available active sites but according to pseudo-second-order model, the adsorption is directly related to square of biosorption sites and to the concentration of metal ions [29,41]. The regression analysis shows that the R^2 value for pseudo-first-order is less than 0.98 but for pseudo-second-order it is equal to 1 suggesting

that kinetic data fulfils the pseudo-second-order kinetics not the pseudo-first-order. In addition to that, the calculated and experimental q_e values considerably varies for pseudo-first-order but quite resembles for pseudo-second-order model, reinforcing the statement above [42]. Result data of pseudo-second-order and pseudo-first-order is given in Table 2.

3.10. Thermodynamics

The metal uptake of the biosorbent is a temperature dependent phenomenon and generally temperature plays as an important factor to be studied while understanding the thermodynamics of the biosorption. Fig. 9a and b illustrate that the metal sorption by the under-discussion plant, *Combretum indicum* adsorption capacity gradually ascended with ascending temperature, that was controlled with the help of a hotplate stirrer (Scilogex SCI340). This increase in the trend is observed probably either by the availability of active and more metal attaching sites with the temperature increase or because of the increased rate of metal ions'

Table 2
Kinetic parameters for the removal of Ni(II) and Cu(II) by C.I

Model	Parameter	Ni(II)	Cu(II)
Pseudo-first-order	k_1 (min ⁻¹)	0.100	0.140
	$q_{e(cal)}$ (mg/g)	3.101	4.241
	$q_{e(exp)}$ (mg/g)	3.679	3.468
	R^2	0.932	0.939
	$D\%$	-15.741	22.201
Pseudo-second-order	k_2 (min ⁻¹)	0.042	0.031
	$q_{e(cal)}$ (mg/g)	4.331	4.372
	$q_{e(exp)}$ (mg/g)	3.679	3.468
	R^2	1	1
	$D\%$	17.690	26.031

(ΔG°), and the change in entropy (ΔS°) [44]. Following are the equations used for the evaluation of the above-mentioned frameworks. This illustrated that what actually is the nature of the procedure of the adsorption:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \tag{4}$$

$$\Delta G^\circ = -RT\ln K_D \tag{5}$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{6}$$

where T is the temperature for the medium K and R represents the universal gas constant (8.314 J/mol K).

Also, the distribution coefficient's value was also calculated by incorporating the following equation, (C_0 and C_e depict initial metal ion and equilibrium concentrations respectively).

$$K_D = \frac{C_0 - C_e}{C_e} \tag{7}$$

diffusion. The same behavior has also been observed in the reported literature of similar research [43].

Different parameters were evaluated while undergoing the thermodynamics of our research. Those included enthalpy variation (ΔH°), variation in Gibbs free energy

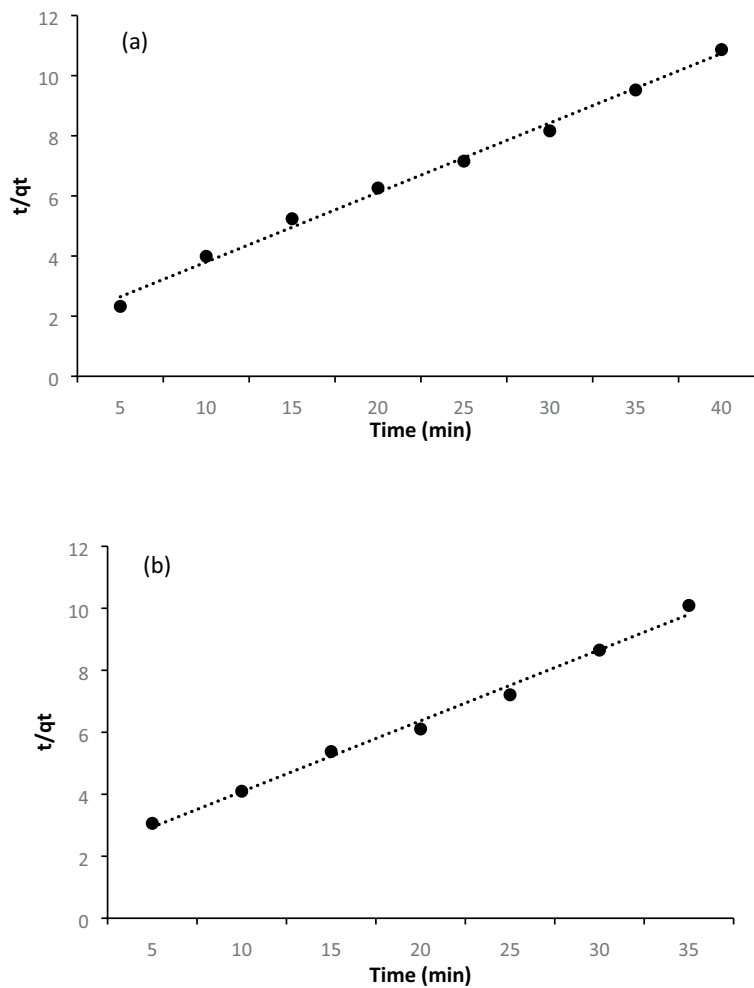


Fig. 8. Pseudo-second-order kinetics for (a) Ni(II) and (b) Cu(II).

Thermodynamic parameters which are obtained from the above equations are given in Table 3. Negative value of Gibbs free energy change (ΔG°) for adsorption of copper and nickel shows the feasibility of process and also indicates that reaction is spontaneous [45]. A positive value of enthalpy change indicates that the process of adsorption is endothermic in nature. This verifies the correct findings of experiment. Positive value of entropy change (ΔS°) shows increase in randomness at solid-solution interface during metal adsorption [28].

3.11. Effect of initial metal ions concentration and equilibrium modeling

The biosorbent and the sorbate relation explains the optimization and scaling of the procedure of the biosorption. To have a complete understanding of the adsorption process we take help from the adsorption isotherms, from non-linear equilibrium models and then also consider the q_{\max} value. The comparative efficiency of different biosorbents for the removal of Ni(II) and Cu(II) has been mentioned in Table 4.

For the evaluation of the adsorption studies of the present studies, Freundlich and Langmuir models were used [46,47]. This nonlinear modelling was implied on the results gathered at equilibrium by varying the starting metal ion concentration at a constant dose of the adsorbent (Fig. 10a and b). The RMSE values obtained as a result were compared to illustrate that which model was supported by which targeted metal ion. Table 5 shows the RMSE values collected from the graphs.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

$$q_e = K_f C_e^{1/n} \quad (9)$$

As shown in Table 5 the value of the q_{\max} informs us about the single-layered capacity and this information is given by Langmuir isotherm model [48]. According to the Langmuir model when the active binding sites of the biosorbent get occupied by the sorbate (metal ion in our research) then there will be no further adhering. So, with the increasing

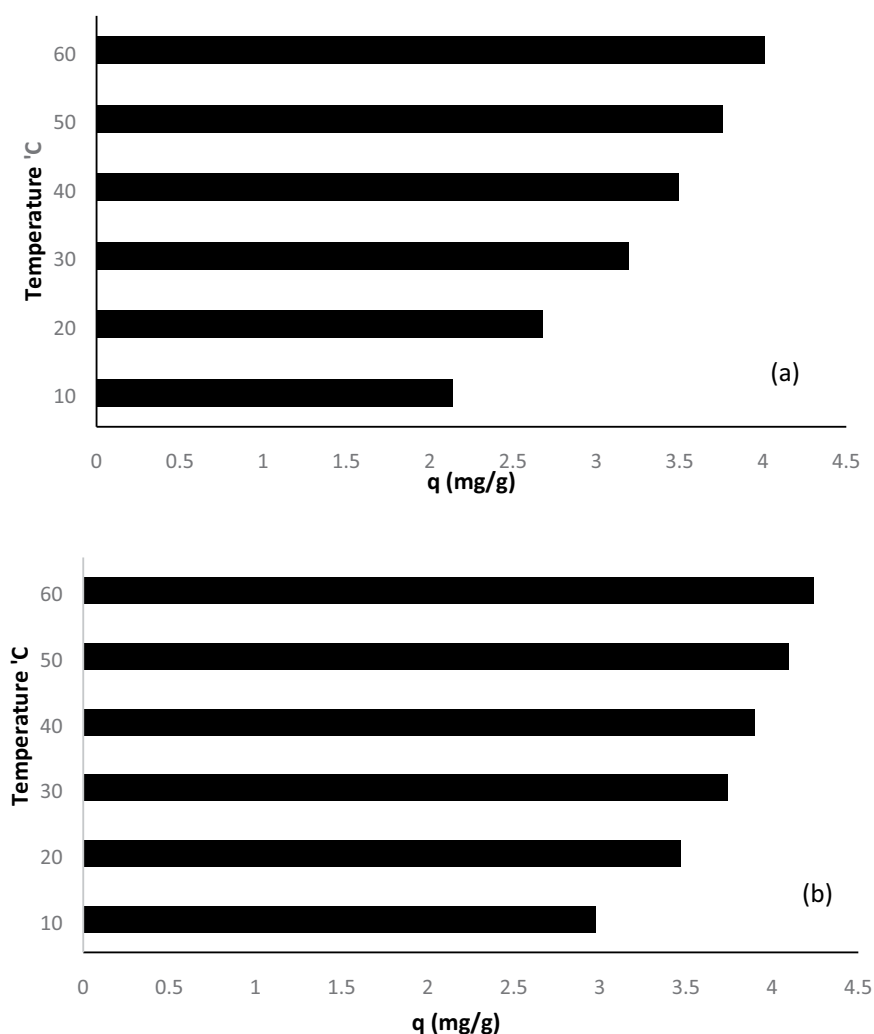


Fig. 9. Temperature studies of (a) Ni(II) adsorption and (b) Cu(II) adsorption.

Table 3
Thermodynamic parameters for the removal of Ni(II) and Cu(II)

Metals	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
Ni(II)	283.160	-0.910	19.990	0.070
	293.160	-1.990		
	303.160	-2.750		
	313.160	-3.300		
	323.160	-4.050		
	333.160	-4.780		
Cu(II)	283.160	0.690	26.010	0.090
	293.160	-0.350		
	303.160	-1.430		
	313.160	-2.200		
	323.160	-2.990		
	333.160	-3.870		

Table 4
Comparison table for the efficiency of biosorbents

Metal	Biosorbent	q_{\max} (mg/g)	References
Cu(II)	Sodium alginate polyvinyl alcohol fungus beads	1.107	[51]
	Neem wood powder	1.90	[52]
	Wheat straw	5.5	[53]
	<i>Araucaria heterophylla</i>	9.250	[21]
	Present study (<i>Combretum indicum</i>)	12.1	
	Banana peels	5.13	[54]
Ni(II)	Pine tree bark	20.58	[55]
	<i>Lagenaria vulgaris</i>	23.18	[56]
	Lemon peel	36.74	[14]
	Present study (<i>Combretum indicum</i>)	27.8	

distance the bonding between sorbate and the binding sites decreases. Active sites on each molecule are independent of the adjacent molecules [45].

While Freundlich model looks into the systematics of the divergent system, according to this model the sorbates are capable of making various layers on the biosorbent's divergent surface. In the present research Cu(II) displayed a greater K_F value as compared to Ni(II), so we can deduce that Cu(II) displayed a greater strength in terms of attractive forces with *Combretum indicum*. Cu(II) and Ni(II) displayed a high ' n ' value, showing strong attraction intensity [49]. The linear interaction between *Combretum indicum* and Ni(II) and Cu(II) is shown by ' n '. The calculated value of n for Ni(II) was 1.303 while for Cu(II) it was 1.796. The value of calculated ' n ' is considered good if it comes in the range of 1–2, indicating a good adsorption intensity [50]. So, the values obtained in the present research were in good accordance to the literature already reported.

Also, the RMSE values obtained from the non-linear equilibrium data displayed that the values in case of both Langmuir and Freundlich models were less than one. But

both Ni(II) and Cu(II) showed more potential towards the Freundlich model in comparison to the other isothermal models, as the RMSE values for the Freundlich model were less than the Langmuir model. The RMSE values for Ni(II) was 0.169 and for Cu(II) it was 0.166 respectively for the afore mentioned model. Table 5 displays a comparative study of the maximum adsorption potential of various biosorbents and *Combretum indicum* for the both in study metal ions.

4. Conclusion

The novel plant *Combretum indicum* has been proved as an excellent biosorbent for the uptake and removal of Ni(II) and Cu(II) from their aqueous solutions. The said biomass was studied and characterized in detail via multiple analyzing techniques including SEM-EDX, TGA, BET surface analysis and FTIR. The data gathered was coherent and in favor of the metal uptake by our targeted adsorbent. The functioning ability of the biosorbent was studied by different processes including change in the metal ion initial concentration,

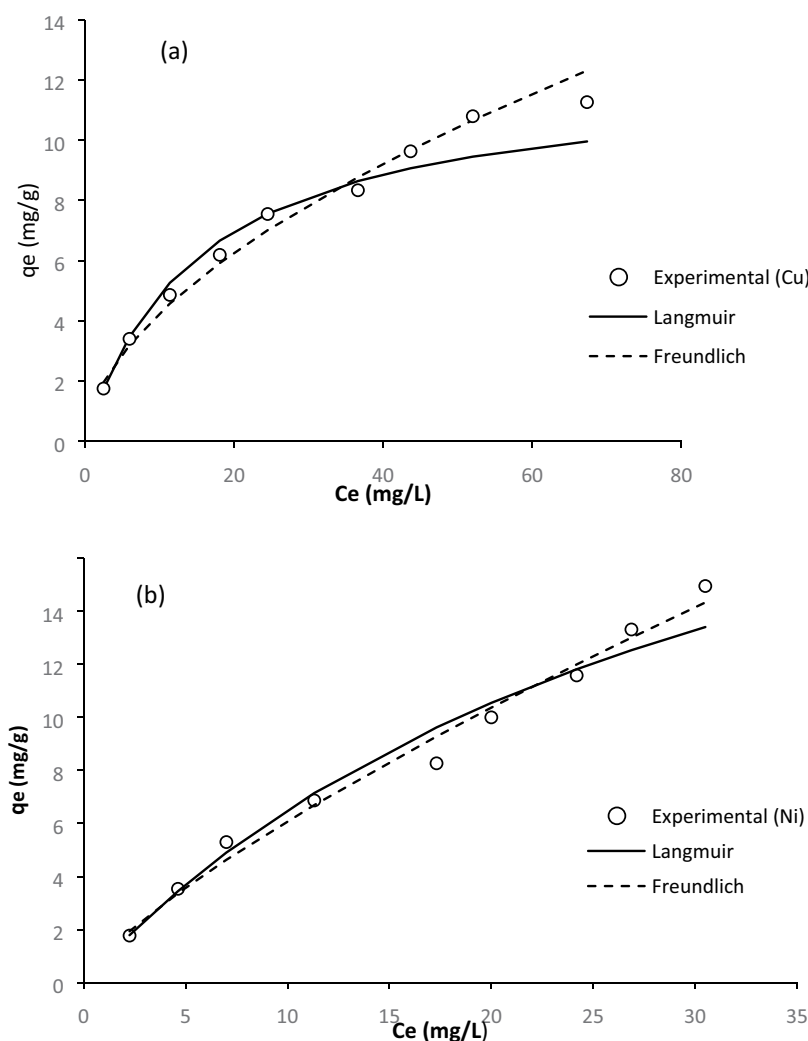


Fig. 10. Non-linear equilibrium studies of (a) Cu(II) and (b) Ni(II).

Table 5
Equilibrium modelling for removal of Ni(II) and Cu(II) by C.I

Model	Parameters	Ni(II)	Cu(II)
Langmuir	q_{\max} (mg/g)	27.811	12.165
	b (L/mg)	0.030	0.067
	R_L	0.619–0.153	0.427–0.076
	R^2	0.996	0.999
	RMSE	0.258	0.287
Freundlich	K_F	1.042	1.181
	n	1.301	1.800
	$1/n$	0.767	0.556
	R^2	0.987	0.987
	RMSE	0.168	0.165

adsorbent dose, time of contact, pH, varying temperature. After the thorough analysis the optimum dosage of C.I. was found to be 0.5 g/50 mL for both adsorbates, the optimum

time of contact was 25 min for Cu(II) and 30 min for Ni(II) metal ions. Optimum pH was found to be acidic. The maximum adsorption capacities for Ni(II) and Cu(II) were found to be 27.8 and 12.1 mg/g respectively. Equilibrium modeling revealed that experimental data fits best in Freundlich's isotherm for both metals. Parameters like R^2 , R_L , and RMSE also support the fitness of Freundlich isotherm. Kinetics modeling shows that data was followed by the pseudo-second-order rate equation indicating the limited rate step mechanism.

Conflict of interest disclosure

Regarding the publication of this article, we have no potential conflict of interest.

Funding statement

Authors are thankful to home department for funding this work.

References

- [1] Q. He, R. Zhu, Q. Chen, Y. Zhu, Y. Yang, J. Du, J. Zhu, H. He, One-pot synthesis of the reduced-charge montmorillonite via molten salts treatment, *Appl. Clay Sci.*, 186 (2020) 105429, doi: 10.1016/j.clay.2019.105429.
- [2] Y. Yang, R. Zhu, Q. Chen, J. Xing, L. Ma, Q. He, J. Fan, Y. Xi, J. Zhu, H. He, Development of novel multifunctional adsorbent by effectively hosting both zwitterionic surfactant and hydrated ferric oxides in montmorillonite, *Sci. Total Environ.*, 774 (2021) 144974, doi: 10.1016/j.scitotenv.2021.144974.
- [3] R. Zhu, T. Wang, J. Zhu, F. Ge, P. Yuan, H. He, Structural and sorptive characteristics of the cetyltrimethylammonium and polyacrylamide modified bentonite, *Chem. Eng. J.*, 160 (2010) 220–225.
- [4] S.A. Abbas, I.M. Ismail, T.M. Mostafa, A.H. Sulaymon, Biosorption of heavy metals: a review, *J. Chem. Sci. Technol.*, 3 (2014) 74–102.
- [5] A. Abdolali, H.H. Ngo, W. Guo, S. Lu, S.-S. Chen, N.C. Nguyen, X. Zhang, J. Wang, Y. Wu, A breakthrough biosorbent in removing heavy metals: equilibrium, kinetic, thermodynamic and mechanism analyses in a lab-scale study, *Sci. Total Environ.*, 542 (2016) 603–611.
- [6] M.R. Rahimzadeh, M.R. Rahimzadeh, S. Kazemi, A.-A. Moghadamnia, Cadmium toxicity and treatment: an update, *Caspian J. Int. Med.*, 8 (2017) 135–145.
- [7] M. Zhao, Y. Xu, C. Zhang, H. Rong, G. Zeng, New trends in removing heavy metals from wastewater, *Appl. Microbiol. Biotechnol.*, 100 (2016) 6509–6518.
- [8] A. Almasi, M. Omid, M. Khodadadian, R. Khamutian, M.B. Gholivand, Lead(II) and cadmium(II) removal from aqueous solution using processed walnut shell: kinetic and equilibrium study, *Toxicol. Environ. Chem.*, 94 (2012) 600–671.
- [9] M.B. Amar, K. Walha, V. Salvadó, Valorisation of pine cone as an efficient biosorbent for the removal of Pb(II), Cd(II), Cu(II), and Cr(VI), *Adsorpt. Sci. Technol.*, 2021 (2021) 6678530, doi: 10.1155/2021/6678530.
- [10] I.S. Bădescu, D. Bulgariu, I. Ahmad, L. Bulgariu, Valorisation possibilities of exhausted biosorbents loaded with metal ions—a review, *J. Environ. Manage.*, 224 (2018) 288–297.
- [11] D. Dhami, P.L. Homagai, Adsorptive removal of malachite green dye from aqueous solution using chemically modified charred and xanthated wheat bran, *J. Nepal Chem. Soc.*, 41 (2020) 103–109.
- [12] E. Savastru, D. Bulgariu, C.-I. Zamfir, L. Bulgariu, Application of *Saccharomyces cerevisiae* in the biosorption of Co(II), Zn(II) and Cu(II) ions from aqueous media, *Water*, 14 (2022) 976, doi: 10.3390/w14060976.
- [13] M. Fawzy, M. Nasr, S. Adel, H. Nagy, S. Helmi, Environmental approach and artificial intelligence for Ni(II) and Cd(II) biosorption from aqueous solution using *Typha domingensis* biomass, *Ecol. Eng.*, 95 (2016) 743–752.
- [14] M. Villen-Guzman, D. Gutierrez-Pinilla, C. Gomez-Lahoz, C. Vereda-Alonso, J.M. Rodriguez-Maroto, B. Arhou, Optimization of Ni(II) biosorption from aqueous solution on modified lemon peel, *Environ. Res.*, 179 (2019) 108849, doi: 10.1016/j.envres.2019.108849.
- [15] U. Shafique, A. Ijaz, M. Salman, W. uz Zaman, N. Jamil, R. Rehman, A. Javaid, Removal of arsenic from water using pine leaves, *J. Taiwan Inst. Chem. Eng.*, 43 (2012) 256–263.
- [16] A. Mishra, A. Dubey, S. Shinghal, Biosorption of chromium(VI) from aqueous solutions using waste plant biomass, *Int. J. Environ. Sci. Technol.*, 12 (2015) 1415–1426.
- [17] M. Fawzy, M. Nasr, S. Adel, S. Helmi, Regression model, artificial neural network, and cost estimation for biosorption of Ni(II)-ions from aqueous solutions by *Potamogeton pectinatus*, *Int. J. Phytorem.*, 20 (2018) 321–329.
- [18] J. Anwar, U. Shafique, Waheed-uz-Zaman, M. Salman, A. Dar, S. Anwar, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana, *Bioresour. Technol.*, 101 (2010) 1752–1755.
- [19] D. Harikishore Kumar Reddy, D.K.V. Ramana, K. Seshiah, A.V.R. Reddy, Biosorption of Ni(II) from aqueous phase by *Moringa oleifera* bark, a low cost biosorbent, *Desalination*, 268 (2011) 150–157.
- [20] S. Liang, X. Guo, Q. Tian, Adsorption of Pb²⁺, Cu²⁺ and Ni²⁺ from aqueous solutions by novel garlic peel adsorbent, *Desal. Water Treat.*, 51 (2013) 7166–7171.
- [21] B. Sarada, M. Krishna Prasad, K. Kishore Kumar, Ch V.R. Murthy, Biosorption of Cd²⁺ by green plant biomass, *Araucaria heterophylla*: characterization, kinetic, isotherm and thermodynamic studies, *Appl. Water Sci.*, 7 (2017) 3483–3496.
- [22] A. Yousaf, M. Salman, R. Rehman, U. Farooq, Detoxification of toxic cations Pb(II) and Cd(II) from liquid phase by employing *Pennisetum glaucum* biowaste: a kinetic investigation, *Int. J. Phytorem.*, 24 (2022) 110–117.
- [23] M. Tariq, U. Farooq, M. Athar, M. Salman, M. Tariq, S. Shahida, Z.H. Farooqi, Lab-scale continuous flow studies for comparative biosorption of cadmium(II) on untreated and xanthated *Ficus religiosa* biomass, *Water Environ. Res.*, 93 (2021) 2681–2695.
- [24] L. Ivanova, P. Vassileva, A. Detcheva, Studies on copper(II) biosorption using a material based on the plant *Thymus vulgaris* L, *Mater. Today: Proc.*, 61 (2022) 1237–1242.
- [25] M. Tukaram Bai, Ch. I.A. Raju, V. Sridevi, N. Chittibabu, P. Venkateswarlu, Lead removal using fallen coffee plant leaves (FCPL) powder: characterization, equilibrium, kinetics and thermodynamic studies, *E3S Web Conf.*, 309 (2021) 01077, doi: 10.1051/e3sconf/202130901077.
- [26] A. Yadav, N. Bagotia, S. Yadav, A.K. Sharma, S. Kumar, Adsorptive studies on the removal of dyes from single and binary systems using *Saccharum munja* plant-based novel functionalized CNT composites, *Environ. Technol. Innovation*, 24 (2021) 102015, doi: 10.1016/j.eti.2021.102015.
- [27] H. Nazir, M. Salman, M. Athar, U. Farooq, A. Wahab, M. Akram, Citric acid functionalized *Bougainvillea spectabilis*: a novel, sustainable, and cost-effective biosorbent for removal of heavy metal (Pb²⁺) from waste water, *Water Air Soil Pollut.*, 230 (2019) 1–16, doi: 10.1007/s11270-019-4360-1.
- [28] M. Salman, R. Rehman, U. Farooq, A. Tahir, L. Mitu, Biosorptive removal of cadmium(II) and copper(II) using microwave-assisted thiourea-modified *Sorghum bicolor* agrowaste, *J. Chem.*, 2020 (2020) 8269643, doi: 10.1155/2020/8269643.
- [29] A.M. Khurram, U. Farooq, M.M. Athar, M. Salman, Biosorption of Cd(II) ions from its aqueous solutions using powdered branches of *Trifolium resupinatum*: equilibrium and kinetics, *Green Chem. Lett. Rev.*, 12 (2019) 217–224.
- [30] W. Hassan, S. Noureen, M. Mustaqeem, T.A. Saleh, S. Zafar, Efficient adsorbent derived from *Haloxylon recurvum* plant for the adsorption of acid brown dye: kinetics, isotherm and thermodynamic optimization, *Surf. Interfaces*, 20 (2020) 100510, doi: 10.1016/j.surfin.2020.100510.
- [31] T. Alp Arici, Highly reusable plant-based biosorbent for the selective methylene blue biosorption from dye mixture in aqueous media, *Int. J. Environ. Sci. Technol.*, 19 (2022) 1849–1860.
- [32] A. Nasrullah, H. Khan, A.S. Khan, Z. Man, N. Muhammad, M.I. Khan, N.M. Abd El-Salam, Potential biosorbent derived from *Calligonum polygonoides* for removal of methylene blue dye from aqueous solution, *Sci. World J.*, 2015 (2015) 562693, doi: 10.1155/2015/562693.
- [33] K.R. Raj, A. Kardam, S. Srivastava, Development of polyethylenimine modified *Zea mays* as a high capacity biosorbent for the removal of As(III) and As(V) from aqueous system, *Int. J. Miner. Process.*, 122 (2013) 66–70.
- [34] B. Chen, M. Yuan, H. Liu, Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent, *J. Hazard. Mater.*, 188 (2011) 436–442.
- [35] W.N.L. dos Santos, D.D. Cavalcante, E.G.P. da Silva, C.F. das Virgens, F. de Souza Dias, Biosorption of Pb(II) and Cd(II) ions by *Agave sisalana* (sisal fiber), *Microchem. J.*, 97 (2011) 269–273.
- [36] S.M. Al-Garni, Biosorption of lead by Gram-ve capsulated and non-capsulated bacteria, *Water SA*, 31 (2005) 345–350.
- [37] C. Karthik, V. Sri Ramkumar, A. Pugazhendhi, K. Gopalakrishnan, P. Indra Arulselvi, Biosorption and biotransformation of Cr(VI) by novel *Cellulosimicrobium funkei* strain AR6, *J. Taiwan Inst. Chem. Eng.*, 70 (2017) 282–290.

- [38] T. Mathimani, A. Pugazhendhi, Utilization of algae for biofuel, bio-products and bio-remediation, *Biocatal. Agric. Biotechnol.*, 17 (2019) 326–330.
- [39] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, John Wiley & Sons Ltd., The Atrium, Southern Gate, Chichester, West Sussex, England, 2004.
- [40] P.K. Pandey, S. Choubey, Y. Verma, M. Pandey, K. Chandrashekhar, Biosorptive removal of arsenic from drinking water, *Bioresour. Technol.*, 100 (2009) 634–637.
- [41] M. Akram, M. Salman, R. Rehman, U. Farooq, S. Tahir, H. Nazir, Kinetic and isothermal investigations of cost-effective sorptive elimination of gentian violet dye from water using *Haplophragma adenophyllum* biowaste, *J. Chem.*, 2021 (2021) 5549536, doi: 10.1155/2021/5549536.
- [42] H. Koyuncu, A.R. Kul, Biosorption study for removal of methylene blue dye from aqueous solution using a novel activated carbon obtained from nonliving lichen (*Pseudevernia furfuracea* (L.) Zopf.), *Surf. Interfaces*, 19 (2020) 100527, doi: 10.1016/j.surfin.2020.100527.
- [43] C. Karthik, S. Barathi, A. Pugazhendhi, V.S. Ramkumar, N.B.D. Thi, P.I. Arulselvi, Evaluation of Cr(VI) reduction mechanism and removal by *Cellulosimicrobium funkei* strain AR8, a novel haloalkaliphilic bacterium, *J. Hazard. Mater.*, 333 (2017) 42–53.
- [44] A. Pugazhendhi, K. Ranganathan, T. Kaliannan, Biosorptive removal of copper(II) by *Bacillus cereus* isolated from contaminated soil of electroplating industry in India, *Water Air Soil Pollut.*, 229 (2018) 76, doi: 10.1007/s11270-018-3734-0.
- [45] S. Dhanarani, E. Viswanathan, P. Piruthiviraj, P. Arivalagan, T. Kaliannan, Comparative study on the biosorption of aluminum by free and immobilized cells of *Bacillus safensis* KTSMBNL 26 isolated from explosive contaminated soil, *J. Taiwan Inst. Chem. Eng.*, 69 (2016) 61–67.
- [46] X.-S. Wang, Y. Qin, Z.-F. Li, Biosorption of zinc from aqueous solutions by rice bran: kinetics and equilibrium studies, *Sep. Sci. Technol.*, 41 (2006) 747–756.
- [47] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, *Water Res.*, 36 (2002) 2304–2318.
- [48] B. Volesky, Biosorption process simulation tools, *Hydrometallurgy*, 71 (2003) 179–190.
- [49] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process Biochem.*, 37 (2002) 1421–1430.
- [50] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, *Ind. Eng. Chem. Fundam.*, 5 (1966) 212–223.
- [51] R. Wang, X.-W. Fan, Y.-Z. Li, Efficient removal of a low concentration of Pb(II), Fe(III) and Cu(II) from simulated drinking water by co-immobilization between low-dosages of metal-resistant/adapted fungus *Penicillium janthinillum* and graphene oxide and activated carbon, *Chemosphere*, 286 (2022) 131591, doi: 10.1016/j.chemosphere.2021.131591.
- [52] N. Arshad, S. Imran, Indigenous waste plant materials: an easy and cost-effective approach for the removal of heavy metals from water, *Curr. Res. Green Sustainable Chem.*, 3 (2020) 100040, doi: 10.1016/j.crgsc.2020.100040.
- [53] Q. Guo, Z. Zang, J. Ma, J. Li, T. Zhou, R. Han, Adsorption of copper ions from solution using xanthate wheat straw, *Water Sci. Technol.*, 82 (2020) 2029–2038.
- [54] S.J. Kakalanga, X.B. Jabulani, O.B. Olutoyin, O.O. Utieyin, Screening of agricultural waste for Ni(II) adsorption: kinetics, equilibrium and thermodynamic studies, *Int. J. Phys. Sci.*, 7 (2012) 2525–2538.
- [55] M.E. Argun, S. Dursun, K. Gur, C. Ozdemir, M. Karatas, S. Dogan, Nickel adsorption on the modified pine tree materials, *Environ. Technol.*, 26 (2005) 479–488.
- [56] M.M. Kostić, M.D. Radović, J.Z. Mitrović, D.V. Bojić, D.D. Milenković, A.L. Bojić, Application of new biosorbent based on chemically modified *Lagenaria vulgaris* shell for the removal of copper(II) from aqueous solutions: effects of operational parameters, *Hemijaska Industrija*, 67 (2013) 559–567.