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A novel biosorbent *B. spectabilisis* stalks leaves for removal of Cd(II) and Cu(II) from wastewater

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ABSTRACT

The present study investigated the use of novel environmental benign ornamental biosorbent *Bougainvillea spectabilisis* for removal of copper and cadmium ions from aqueous medium. Raw biosorbent and metal loaded biosorbent were characterized by FTIR. Slight shift in peak(s) of hydroxyl, carbonyl and alkyl group affirms that these groups are responsible for metal attachment. Different process parameters *i.e.* varying initial metal ion concentration, pH, contact time and temperature were studied and optimized. Thermodynamic study proves the feasibility of process showing that process is endothermic and spontaneous. Pseudo-second order kinetic model was found to be followed by both metal ions biosorption process. Non-linear equilibrium study showed fitness of Langmuir model for Cd(II) and Freundlich model for Cu(II) equilibrium data. The study indicated that *Bougenvillae Spectobilisis* can be effectively be used for heavy metal remediation.

Keywords: *Bougenvillae spectobilisis*; Lead; Cadmium; Non-linear equilibrium; Thermodynamics; Pseudo-second order kinetic

1. Introduction

This world is going to be an industrial world but the results are not environmental benign. Industries are the main source of heavy metal pollution in environment. These heavy metals become part of ground water due to peculation of waste water through soil [1] thus enters in our body. Toxic effects of heavy metals are determined by their intensity, period of contact and their frequency [2]. Cadmium is a toxic heavy metal emanating from industries and agricultural sources [3]. It gets entry in water resources through metal extraction, industrial processing including smelting, electroplating, plasticizers and batteries [4]. The effect of cadmium on health is determined by several factors like nutritional habits as well as deficiency of iron in body. It retains in kidney half time 10–30 years. It is nephrotoxic, cause renal failure, bone impairment and carcinogenic [3]. It has also been found as factor causing hypertension, testicular tumour, arteriosclerosis, stunted growth [5], change in structure of enzyme as well as impairment of its catalytic activity [6].

Copper is found in form of sulphates and oxides in the nature mostly in rocks. In water its main industrial resources are paints and pigment industry, petroleum industry, steel works, electroplating, etching and foundries [7,8]. Copper is essential element for body but its excessive intake can cause serious problems for health. According to WHO and EU maximum permissible limit in potable water for Cu(II) is 1.0 and 2.0 mg/L respectively [9] while in industrial effluent the permissible value of Cu(II) is 1.3 mg/L according to USEPA (USEPA 2002). Copper cause gastrointestinal infections [10,11] weakness, lethargy, anorexid [12,13] liver and kidney diseases [14].

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Removal of heavy metals by biosorption process using dead biomass is gaining much attention now a days as alternative method than conventional techniques [15]. Number of authors has been reviewed on the efficiency of alive as well as dead organic materials for purpose of metal biosorption [4,16,17]. In addition to aesthetic purpose ornamental plants play a vital role in landscape, windbreak, water management as well as shelter belts of gardens [18].

Present study focused on the use of a novel biosorbent *Bougainvillea spectabilisis* for the removal of Cu(II) and Cd(II) ions. It is an ornamental and draught tolerant plant. It requires a little or no care because it is a pest free plant. It remains evergreen in the areas of rainfall or may be deciduous in the dry areas. It require very less amount of water to grow. It is drought tolerant and grows in areas of warm climate conditions like in Pakistan.

2. Material and methods

2.1. Preparation of biomass

Stalks along with leaves of *Bougainvillea spectabilisis* were collected from nearby local area of Lahore, Pakistan. Biomass then grounded and sieved through 80 mesh size. Water soluble impurities and dust particles were washed by using distilled water several times. Then mass was dried in oven at 70°C and stored in a dry place for further use.

2.2. Characterization of biomass

Various functional groups analysis on *Bougainvillea spectabilisis* was carried out using FTIR Spectrophotometer by KBr disc method (Perkin Elmer RX-1 spectrum). The biosorbent was subjected to FTIR analysis before and after biosorption of Cu^{2+} and Cd^{2+} ions.

2.3. Preparation of cadmium and copper solutions

Cd(II) and Cu(II) stock solution of 1000 ppm were prepared with distilled water using cadmium nitrate and copper sulphate of analytical grade (Merck) respectively. Test standards of different concentrations were prepared by the dilution of stock solutions of cadmium and copper.

2.4. Technique of analysis and apparatus

Analysis of Cd(II) and Cu(II) solutions was performed by atomic absorption spectrophotometer (Perkin Elmer Model-A Analyst 100) at 228.8 and 324.8 nm, respectively.

Batch experiments were carried out in 250 ml conical flask placing on orbital shaker (VORTEX Model no: OSM-747). pH of solutions was adjusted using 0.1 M NaOH and 0.1 M HCl solutions with help of digital pH meter (ADWA, 130).

2.5. Batch stirred experiments

Series of experiments were carried out using 50 ppm of the cadmium and chromium solutions and noted the effect of different parameters *i.e.* adsorption dose, pH, temperature, time of contact, initial metal ion concentration for the removal of heavy metal from solution 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 Cd and Cu were checked by changing parameters such as pH (1–8), time of contact (5–45 min), temperature (10–70°C)and initial metal ions concentration (20–180 ppm). For determining the concentration of Cd and Cu in solution, the processed solutions were filtered and examined by using flame atomic absorption spectrophotometer. The values then quantified against standard solutions of respective metal ions. Sorption capacity of metal ions was calculated using formula

$$q_e = \frac{C_o - C_e}{m} \times V \tag{1}$$

where 'm (mg)' is the biosorbent dose, q_e (mg/g) represents the uptake capacity of biosorbent, C_o (mg/L) is the initial concentration and C_e (mg/L) is the equilibrium concentration of the metal ions and 'V (mL)' is the volume of solution under study.

2.3. Equilibrium study

Solutions of Cd and Cu of certain concentrations from (20–180 ppm) were prepared in 100 mL measuring flask and 50 mL of each was taken under optimum conditions obtained from experimental procedure and studies for adsorption of these ions. Equilibrium models including Langmuir model and Freundlich model were applied on the obtained values for evaluation of equilibrium data and their optimum parameters were calculated from respective plotation. Microsoft Excel 2013 software was used for linear and nonlinear plotting. All experiments were performed in triplicate and mean values are reported. Glass ware interference was checked by the blank biosorption experiments for Cu(II) and Cd(II) ions. No interference was observed due to glass ware in adsorption. Root mean square error (RMSE)and regression analysis R^2 have been performed to investigate the error of predicted models and stability of mathematical models. RMSE is calculated by dividing the sum of squares of difference between experimental data q_e (exp) and model predicted q_e(cal) for metal adsorption to number of data points (N) then square root of this obtained data was taken.

$$RMSE = \sqrt{\frac{\Sigma\left(q_{e(cal)} - q_{e(\exp)}\right)^2}{N}} \tag{2}$$

3. Result and discussion

3.1. Characterization

FTIR spectra of metal loaded and unloaded *Bougainvillea spectabilisis* was obtained that gave the information about various functional groups that may be the binding sites for metal ions.

FTIR identified the presence of Hydroxyl (–OH) group, Carbonyl (C=O) group, Alkyl (C-H) group and Ether (C-O-C) group. Their peaks are described in Table 1 [19]

Table 1
Main functional groups in *Bougainvillea spectabilisis* indicated by FTIR [19]

Functional Groups	Peaks (cm^{-1})
Hydroxyl group	3312
Carbonyl group	1632
Alkyl group	1421
Ether group	1027

Fig.1. For biomass loaded with metals i.e. Cu(II) and Cd(II), small shifts are observed in peak positions for hydroxyl (–OH) group, carbonyl (C=O) group and alkyl (C-H) group. These shifts show the attachment of metal ions with the functional groups –O containing donor atom. The result exhibit the presence of different functional groups which are responsible for the metal attachment on *Bougainvillea* and removal from the waste water.

3.2. Effect of adsorption dose

The effect of adsorbent dose was checked through series of experiments conducted by varying the concentration of the biosorbent. The obtained results are shown in Fig. 2. Adsorption capacity increases with the increase in concentration of the biosorbent, however, decreasing after the saturation point. Increase in adsorption capacity shows the availability of more active sites for metal attachment, however, after a certain value of biosorbent the decrease in adsorption capacity points towards the decrease in active sites due to coagulation or aggregation of the biosorbent [20,21]. This step tells us the quantitative uptake capacity of biosorbent for metals that is different for every metal.

At lower concentration of biosorbent, the ratio of available sites on the material for lower metal ions concentration is high, so all the Cu(II) and Cd(II) ions are attached to the binding sites on biosorbent [22]. On the other hand, when the biosorbent concentration increases, this ratio decreases, which leads to less attachment of metal ions with biosorbent, as metal ion has occupied the maximum binding sites on biomass.

3.3. Effect of pH

pH of solution plays an important role in metal uptake capacity of biosorbent. It tells about the degree of ionization, metal ions nature as well as charge on the adsorbent [23]. It effects on number of unsaturated sites on biosorbent. Experiments were performed varying the pH of solution from 1 to 10 keeping the rest of factors constant. Optimum value of pH is slightly acidic i.e. between 5–6 (exhibited in Fig. 3). Increase in percentage removal with increase in pH is due to deprotonation of some binding sites making them available for metal attraction. While after a certain limit the metal uptake capacity of adsorbent starts decrease. It shows the formation of metal hydroxides due to which metal ions start to precipitate out. At low pH the repulsion of cation with protonated sites of adsorbent decrease the adsorption capacity. Almost similar trends have been observed and reported for different biosorbents [24–26].

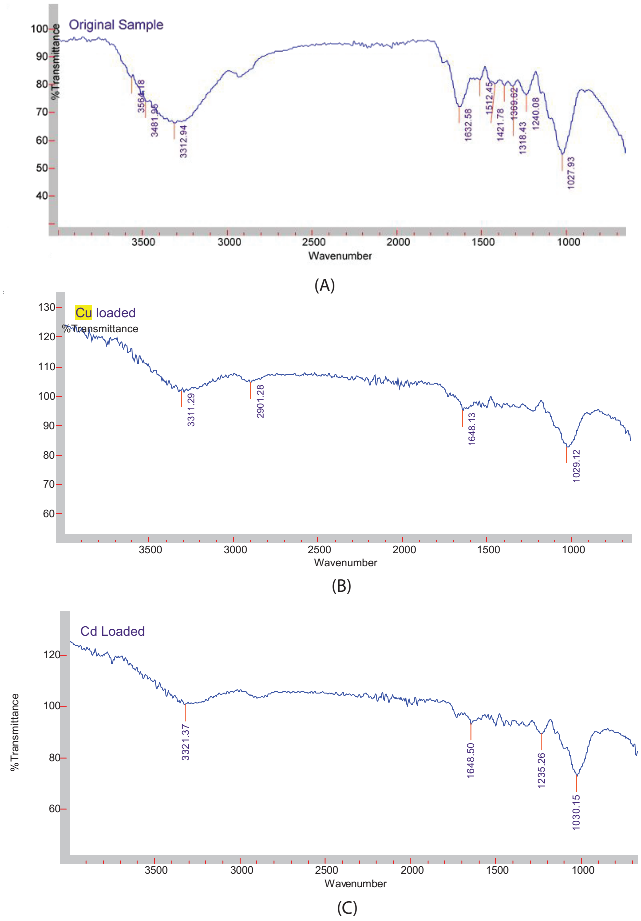

Fig. 1. (a) FTIR spectrum of *Bougainvillea spectabilisis* biomass. (b) FTIR spectrum of Copper loaded *Bougainvillea spectabilisis* biomass. (c) FTIR spectrum of Cadmium loaded *Bougainvillea spectabilisis* biomass.

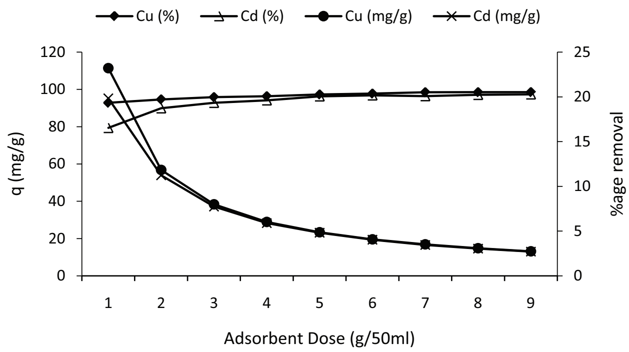

Fig. 2. Effect of *Bougainvillea spectabilisis* dose on removal of Cu^{+2} and Cd^{2+} ions (initial conc. = 50 mg/L, time = 30 min, pH= 6, stirring speed= 125 rpm).

3.4. Adsorption kinetics

Optimum time for maximum uptake of metal by adsorbent keeping the other factors constant is studied and explained in Fig. 4.

The Fig. 4 indicates that adsorption increases with the increase in time of contact,however after a certain interval of time it becomes constant. For Cu(II) removal the equilibrium time occurs in 25 min,while for Cd(II) removal occurs in 35 min. At equilibrium, maximum binding sites adsorb the metal ions, and after this period no further binding occurs due to repulsive forces development between particles of solute in bulk phase and in solid phase [27]. In addition, another factor of prime importance is the accessibility of metal ions to biosorbent surface. Biosorption kinetics have been studied by employing the most popular pseudo-first order [PFO, Eq. (3)] and pseudo second order [PSO, Eq. (4)] kinetic models [28,29].

$$\ln\left(q_e - q_t\right) = lnq_e - K_1 t \quad (3)$$

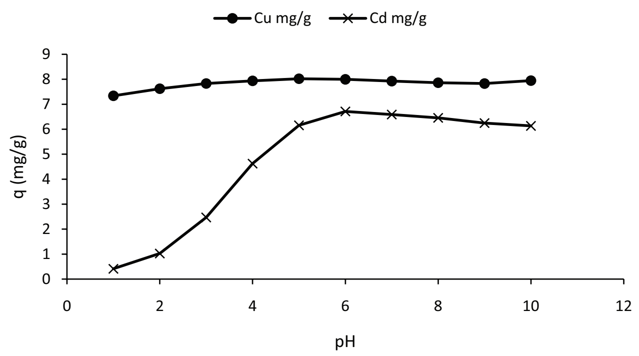

Fig. 3. Effect of pH on biosorption of Cu^{2+} and Cd^{2+} ions on *Bougainvillea spectabilisis* (initial conc. = 50 mg/L, dose = 300 mg/50 ml, time = 30 min, pH = 6, stirring speed = 125 rpm).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e (mg/g) and q_t (mg/g) is the uptake capacity of biosorbent at equilibrium and instantaneous time *t*, respectively. K_1 (min^{-1}) and K_2 (g/mg/min) are the constants of pseudo-first order 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. The regression analysis shows that the R^2 value for PFO is less than 0.98 but for PSO it is equal to 1 suggesting that kinetic data fulfils the PSO kinetics not the PFO. In addition to that, the calculated and experimental q_e values considerably varies for PFO but quite resembles for PSO model, reinforcing the statement above. Result data of PSO and PFO is given in Table 2.

3.5. Effect of temperature: study of thermodynamics

In biosorption process, temperature plays a vital role so thermodynamic study is of prime importance to understand the process. Uptake capacity of *Bougainvillea spectabilisis* for Cu(II) and Cd(II) as function of temperature is illustrated in Fig. 5. The adsorption capacity increases with the increase in temperature up to a certain level, which illustrates that this phenomenon or reaction is endothermic. Biosorption increases with the increase in temperature may either be due to increase in active sites for metal binding, or due to increase in diffusion rate of metal ions. Similar findings have been reported in previous studies of this type

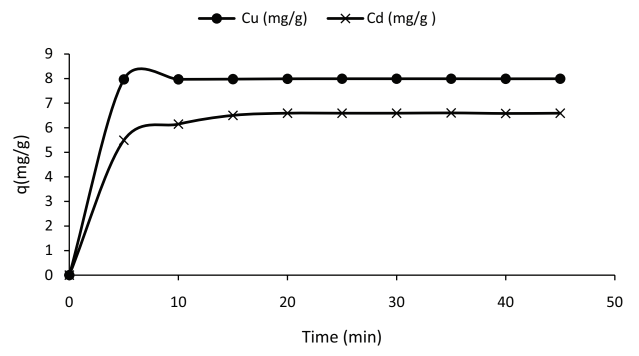

Fig. 4. Effect of time on biosorption of Cu^{2+} and Cd^{2+} ions on *Bougainvillea spectabilisis* (initial conc. = 50 mg/L, dose = 300 mg/50 ml, time = 30 min, pH = 6, stirring speed = 125 rpm).

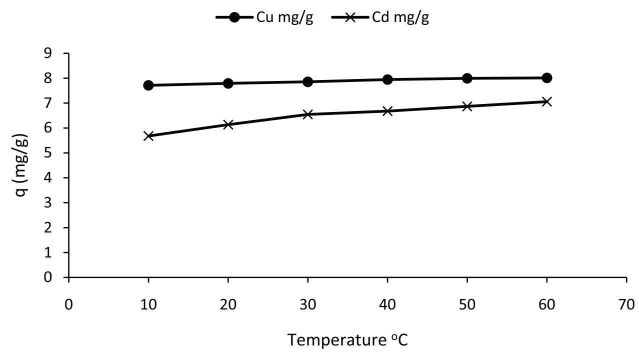

Fig. 5. Effect of temperature on biosorption of Cu^{2+} and Cd^{2+} ions on *Bougainvillea spectabilisis* (initial conc. = 50 mg/L, dose = 300 mg /50 ml, time = 30 min, pH = 6, stirring speed = 125 rpm).

Table 2
Kinetic study results for biosorption of Cu^{2+} and Cd^{2+} on *Bougainvillea spectabilisis*

Adsorbates	PFO Model			*q* (exp) (mg/g)	PSO Model		
	K_1 (min^{-1})	q_e (cal) mg/g	R^2		K_2 (mg/g/min)	q_e (cal) mg/g	R^2
Cu^{2+}	0.5324	3.85	0.6558	7.993205	5.0403	8	1
Cd^{2+}	0.2516	1.2797	0.9723	7.820261	0.7468	7.85546	1

of phenomenon [30]. Thermodynamic study includes the parameters like Gibbs free energy change (ΔG°), Enthalpy change (ΔH°), Entropy change (ΔS°). These parameters portray the nature of the adsorption process. These parameters are calculated using the following equations [31].

$$\Delta Go = -RT\ln K_D \tag{5}$$

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

where R is universal gas constant (8.314 j/mol^{-1} K^{-1}), T is temperature of medium (K) and K_D is the adsorption distribution coefficient which is calculated from following equation:

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

where C_o is initial metal ions concentration and C_e is concentration of metal ions at equilibrium.

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 cadmium shows the feasibility of process and also indicates that reaction is spontaneous [32]. A positive vale 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 Cu(II) and Cd(II) adsorption [33].

3.6. Equilibrium modeling: studying the effect of initial metal ions concentration on adsorption

Scaling and optimization of biosorption process majorly depends upon the interaction between biosorbent and sorbate. The adsorption process can be well explained by equilibrium models or adsorption isotherms. This interaction or relation between adsorbent and adsorbate is well explained after the establishment of equilibrium. For this purpose, Langmuir [34] [Eq. (8)] and Freundlich [35] [Eq. (9)] models in non-linear fashion were applied on the equilibrium data obtained using different initial metal ions concentration at a fixed adsorbent dose and comparison was done using their RMSE value. RMSE value obtained from respective plot (Fig. 6) is exhibited in Table 4.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{8}$$

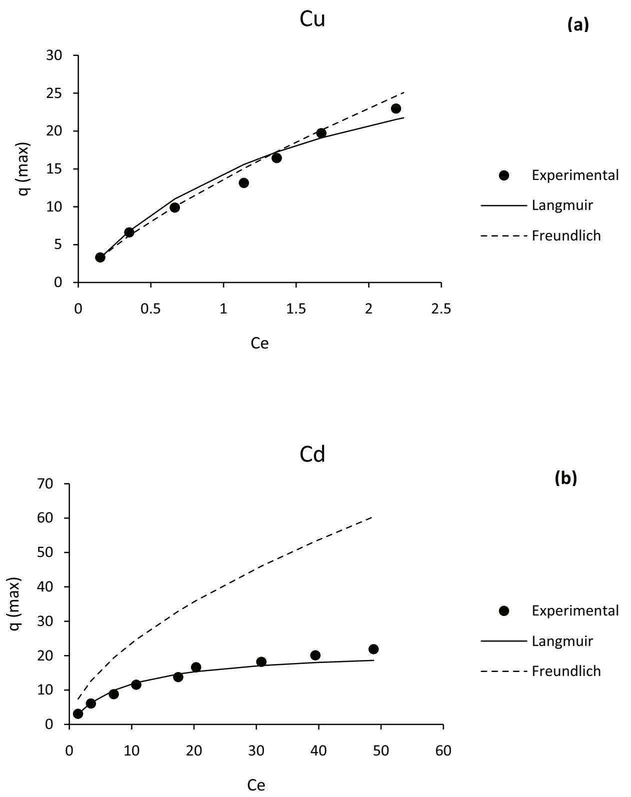

Fig. 6. Non-linear isotherm plots for Cu^{2+} (a) and Cd^{2+}(b) for Langmuir and Freundlich model.

Table 3
Thermodynamic Parameters for Cu^{2+} and Cd^{2+} biosorption on *Bougainvillea spectabilisis*

Adsorbates	ΔG° (KJ/mol)			ΔH° (KJ/mol)	ΔS° (KJ/mol)
	30°	40°	50°		
Cu^{2+}	–7.03835	–7.83619	–8.48019	11.52	0.061
Cd^{2+}	–3.26911	–3.63112	–4.1475	14.41	0.057

Table 4
Parameters of non-linear isotherm for Cu^{2+} and Cd^{2+} biosorption

Adsorbates	Langmuir parameters				Freundlich parameters			
	q_{max} (mg/g)	R^2	b (dm^3/g)	RMSE	R^2	K_F	n	RMSE
Cu^{2+}	36.76	0.9912	0.646	1.078385	0.985	13.65	1.326	0.61014
Cd^{2+}	21.92	0.9941	0.1157	0.941393	0.9921	6.0729	1.692	6.069066

Table 5
Comparison of biosorption capacity of *Bougainvillea spectabilisis* with other materials

Biosorbent	Metal ion	q_{max} mg/g	References
Coconut copra meal	Cd^{2+}	4.99	[40]
P. glaucum	Cd^{2+}	5.55	[30]
Banana peels	Cd^{2+}	5.71	[41]
Bougainvillea spectabilisis	Cd^{2+}	21.92	Present Study
Gardenia jasminoides	Cd^{2+}	48.54	[15]
Eriobotrya japonica leaves	Cd^{2+}	48.78	[42]
Barley straw	Cu^{2+}	4.64	[43]
Thuja orientalis	Cu^{2+}	19.23	[44]
Bougainvillea spectabilisis	Cu^{2+}	36.76	Present Study
Chitosan-crosslinked GLA	Cu^{2+}	59.67	[45]
Chitosan-crosslinked ECH	Cu^{2+}	62.47	[45]

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

Langmuir isotherm model gives information about monolayer capacity (q_{max}) of biosorbent (Table 4) [36]. According to Langmuir isotherm when one metal ion occupies the binding sites on adsorbent no further attachment occurs, and the intermolecular forces between active sites and adsorbent decreases with increase in distance. Each binding site behave independent of neighboring molecule [37].

Freundlich isotherm is used to describe the behavior of heterogeneous system according to which metal ion form multiple layers on the heterogeneous surface of the sorbent. A higher value of K_F for Cu(II) ions shows strong strength of interaction between sorbate and sorbent. Cd(II) and Cu(II) ions showed higher n value indicating strong interaction intensity [38]. "n" shows linear relation between adsorption and metal containing solution. Value of "n" between 2 to 10 shows better intensity while 1 to 2 shows good and >1 shows average adsorption intensity [39]. Value of n for Cd(II) ions was 1.692 while for Cu(II) ions it was 1.326 indicating that both have good intensity of adsorption. Less than 1 value of RMSE is shown by Cu(II) ions (0.61014) for Freundlich model and by Cd(II) ions (0.94139) for Langmuir model.

It is concluded from above discussion that Langmuir model is fit well in case of Cd(II) and Freundlich model fits for Cu(II) as compared to other isothermal models. A comparison of maximum sorption capacity of present study of Cd(II) and Cu(II) interacting with *Bougainvillea spectabilisis* and other biosorbents is illustrated in Table 5.

4. Conclusion

The present study focused on the use of *B. spectabilisis* for biosorptive removal of Cu(II) and Cd(II) ions from aqueous medium. The results indicate an effective removal of metal ions between 5–6 pH range and optimum time for equilibrium of 25–35 min. The equilibrium study showed that the maximum uptake capacity of absorbent for Cu(II) is 36.76 mg/g and for Cd(II) is 21.92 mg/g. The non-linear study of equilibrium process proves that Langmuir model fitted well for the Cd(II) showing less RMSE value i.e. 0.941393 while Freundlich model is followed more by Cu(II) showing RMSE value 0.61014. Above statement also gets potential by "n" value that proves higher intensity of adsorption. Kinetic study indicates that the adsorption mechanism is followed by pseudo-second-order kinetic model. Moreover, the thermodynamics parameters showed that process is feasible, spontaneous and endothermic in nature. So, *Bougainvillea spectabilisis* is proved to be efficient, cost effective and environmental benign adsorbent proving efficient heavy metal removal behaviour.

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