Removal of Cadmium(II) from Aqueous Solutions by using Chemically Modified Pods of Dalbergia Sissoo

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ABSTRACT

The rapid increase in industrialization has resulted in water pollution leading to severe health hazards. The effluents consisting of heavy metals are treated through the conventional methods which have one or another disadvantages like high cost, difficulty in regeneration, long time of action, high energy consumption and sludge formation. The development of alternative low cost technologies for waste water treatment have been in progress. The work is being done on study of adsorption of heavy metals on various low cost biomaterials since last few years which have been found to be of great potential for sequestering heavy metals from aqueous streams with low concentration and high volume. The present study has been made on Cd(II) removal from aqueous solutions by using NaOH treated pods of Dalbergia sissoo as abundantly available biomaterial. The kinetic and equilibrium studies have been made. The effect of various factors (such as pH, stirring speed, initial metal ion conc. contact time, adsorbent dose) have been found in batch experiments in their significant ranges. Adsorption behaviour has been studied by applying Freundlich and Langmuir isotherms. Thermodynamic studies have also been made through the experiments at various temperatures. The pods of Dalbergia sissoo in their chemically modified form show better results for sequestering Cd(II) from aqueous solution as compared with its raw form and can suitably be used as a cost effective alternative of commercially available adsorbents.

Keywords - Biosorption, biomaterial, heavy metals, wastewater.

I. INTRODUCTION

Increasing demand of the heavy metals has put the world in a challenge to save the environment and the health hazards thereof. Industrial emissions intentionally or accidentally through chemical or oil spills release the organic as well as inorganic compounds to the environment [1]. The industries like paints, alloys and metals, mining, electroplating, batteries, paper, tanneries, petrochemicals, automobile etc. are responsible to release the heavy metals hich get accumulated into the water bodies and has created a serious problem to be handled worldwide for sustainability. Out of these metals, Cadmium is one of the most important metals which is used widely but has high toxicity. Major industries causing pollution due to Cd(II) are Cd/Ni batteries, plastic, electroplating, metallurgical processes, pesticides, pigments, fertilizers etc. The health impacts because of Cd(II) have been reported as high blood pressure, bone fraction, kidney damage, renal disorder, damage to red blood cells etc. [2]. History has reported a classical example of the hazard 'Itai-Itai desease' caused by Cd(II) contamination in Jintsu river basin in Japan in 1912. The permissible limits for Cd(II) are 0.01 mg/L and 0.005 mg/L in wastewater and in drinking water respectively (as described by WHO) [2].

A number of technologies for removal and recovery of heavy metals from the aqueous streams have been developed. Conventional technologies for the purpose include chemical precipitation [3], flotation [4], ion exchange, adsorption on minerals, chelating resin [5-7], membrane separation, electrolysis, reverse osmosis [8]. These conventional techniques have many limitations and disadvantages such as cost, sludge formation, availability and reusability. In the developing countries which rely upon unskilled labour and less on automation, the prime need is to explore simple but effective inexpensive solution for such waste water treatment. Adsorption is found to be a better technique to overcome the limitations. Adsorption on activated carbon [9-11] and activated carbon obtained from agricultural waste material [12, 13] are widely used. However, the use of agricultural waste materials/ cellulosic biomaterials as adsorbents has been studied during last few decades which reduces the cost to further extent providing an almost comparable efficiency. Biosorption using low cost sorbents has been found considerably effective for removal and recovery of heavy metals from aqueous streams [14]. Many of cellulosic materials found in nature have been used for the purpose. Some of these are plant/ agricultural wastes such as tea waste [15], coffee beans [16], coffee husks [17], mungbean husk [18], peels of lemon, orange, grapefruit, apple, apple kernel, grape [19] etc. Chemical modification of agricultural by-products could enhance their natural capacity for the uptake of metal ions [20]. Corn stalk treated with acrylonitrle [21], corncob treated with citric acid [22], rice husk treated with nitric acid and potassium carbonate [23], bagasse treated with sulfuric acid [6], polyacrylamide grafted rice (*Oryza sativa*) husk and (*Tectona grandis*) saw dust [24], thiolated cassava fiber, cassava bark waste and rice husk [25-27], esterified coir pith, rice husk, lemon and saw dust [28-31], have been studied for sequestering the metals from aqueous solutions.

In the present study, pods of Dalbergia Sissoo, chemically treated with NaOH, have been tried to observe its potential and capacity for removal of Cd(II) from water stream. Kinetic and equilibrium studies have been made for Cd(II) sorption on this modified biomaterial. Through the batch experiments, effects of various parameters affecting the adsorption of cadmium on biomaterial such as pH, stirring speed, initial metal ion conc. contact time, adsorbent dose have been investigated.

II. EXPERIMENTAL

2.1. Preparation of Adsorbent

Pods of Dalbergia Sissoo were collected from the trees at Longowal, Punjab (India), dried in sun for about 10 hours and then at 110^0C in hot air oven for 10-12 hours. After grinding, the biomaterial was washed with double distilled water. The material was again dried at 110^oC for 24 hours and then sieved to get 120-150 micron size particles. The raw powder is then treated with 0.1M NaOH solution (in the ratio of 1:40) by placing the biomaterial in NaOH solution for 24 hours. After filtering the biomaterial is washed with demineralised water and dried for 24 hours in hot air oven at 100^0C and then packed in sealed polyethylene bags for further use.

2.2. Chemicals Used

Synthetic solutions of cadmium ions have been used for performing the experiments. Analytical grade chemicals were used for all experimental purpose. For preparation of a stock solution of cadmium concentration as 1000 mg/l, Cadmium nitrate (Merck) in double distilled water was used. To obtain solutions of desired Cd (II) ion concentrations by diluting stock solution, double distilled water was used. 0.01M HCl and 0.01M NaOH were prepared for adjustment of pH of the solutions. For NaOH treatment of biomaterial purified NaOH (Merck) (AR Grade) has been used.

2.3. Instruments Used

In the aqueous solutions, all pH and Cd(II) ion concentrations were measured by using pH/ISE Meter (ThermoScientific Orion, model : DUAL STAR). Weighing balance with least count 0.001 gm has been used.

2.4. Characterization of biosorbent

The biosorbent material was characterized by proximate analysis to find the moisture content, ash content and the loss of weight at various temperatures upto 500^0C. The functional groups available over the biosorbent were detected by using FTIR (Fourier Transform Infrared Analysis).

2.5. Batch Experiments

Batch experiments were performed to study the adsorption of cadmium from aqueous solutions at various pH (2- 8), initial metal ion conc. (10 mg/l – 400 mg/l), stirring speed (50 rpm – 250 rpm), adsorbent dose (400mg - 2000mg) for 60 minutes contact time in the 300 mL glass BOD bottles on the Orbital Shaker. Through the preliminary experiments, the suitable ranges of each parameter were found and the final experiments were performed for studying effect of various parameters mentioned above keeping other parameters constants. After setting pH of the solution (100 ml.) with known initial conc. of metal ion, desired dose of biosorbent was added and solution was kept on stirring on orbital shaker at specific speed for desired time and temperature. At the end, the solution was decanted off and filtered. Residual concentration of Cd(II) in the solution was found by use of pH/ISE Meter. All experiments were replicated thrice.

2.6. Equilibrium Studies

The relationship between equilibrium concentration of the metal ion in solution (C_e, mg/l) and the amount of metal adsorbed per unit mass of biosorbent (x/m, mg/g) is represented by Freundlich adsorption isotherm :

$$\ln\left(\frac{x}{m}\right) = \ln K_f + \frac{1}{n}\ln C_e$$

where n & K_f are Freundlich parameters representing extent of adsorption and the adsorption capacity of biosorbent towards the metal respectively. Plot of log(x/m) vs. log C_e for various initial conc. of Cd(II) was drawn to find above parameters.

Langmuir isotherm expresses the monolayer adsorption over a surface with finite number of identical sites resulting in uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. It is given as :

$$\frac{C_e}{x/m} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

where b and Q_0 are Langmuir constants corresponding to energy of adsorption and adsorption capacity respectively. Linear graph between $C_e/(x/m)$ vs. C_e is drawn to find these parameters.

3.8 Kinetic Studies

Kinetic studies for the adsorption of Cd(II) on NaOH treated pods of dalbergia sissoo has been carried out by using the rate equation [25] :

$$R = K\,C^n$$

where R is rate of adsorption, K is rate constant, C is concentration and n is the order of the reaction.

Lagergren first order equation is given as :

$$\log (q_e - q) = \log q_e - \frac{K_{ad}\,t}{2.303}$$

where K_{ad} (L min^{-1}) is first order rate constant of adsorbent, q and q_e are amount of metal ions adsorbed (mg/g) at time t (min) and equilibrium time respectively. Linear plots of log (q_e-q) vs time can be analysed to find the parameters.

Pseudo second order equation (Ho and McKay's) is given as :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is equilibrium rate constant of pseudo-second order adsorption (g mg^{-1} min^{-1}). The slopes and intercepts of plots t/q_t versus t is used to calculate the pseudo second order rate constants k_2 and q_e

III. RESULTS AND DISCUSSION

3.1. FTIR analysis

Infrared spectrum of the biomaterial after taking up Cd(II) from aqueous solution showed bands at 3408.67 cm^{-1} resulting in presence of surface hydroxyl groups and the peak observed at 1637.72 cm^{-1} describe the presence of non-ionic carboxyl group showing stretch of amide C=O bonds. The similar bands at 3565.27cm^{-1} and 1608.79 cm^{-1} have been found in the IR spectra of raw form of biomaterial unloaded with Cd(II). The treatment with NaOH enhances the charge because of –OH group over the surface and because of which the uptake capacity of NaOH treated biomaterial towards Cd(II) have been found to be increased.

3.2. Effect of initial pH

The effect of pH has been examined in the range from 2 to 8 for Cd(II) removal by NaOH treated pods of dalbergia sissoo at all other parameters as constant (initial concentration of Cd(II) 50mg/l; stirring speed 200 rpm; contact time 60 min, adsorbent dose 1200 mg/100mL, temperature 25 ± 1^0C). Percent adsorption increased on increase in pH from 2.3 to 6 and then after pH 6 upto 8 the percent removal has been found to be constant. At pH 8, precipitation of cadmium occurred. As shown in Fig. 1, the percent adsorption is found to be maximum at pH 6. The sharp decline in percent removal below pH 3 shows the possibility of desorption of Cd(II) at lower pH and hereby regeneration of the biomaterial. At lower pH, the low level of adsorption may be because of neutralization of surface charge due to -OH ions.

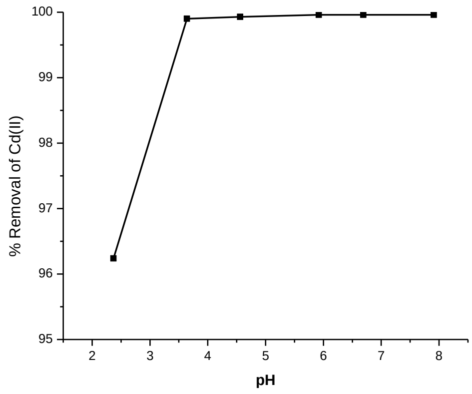


Fig. 1: Effect of initial pH on adsorption of Cd(II) from aqueous solution by using NaOH treated pods of dalbergia sissoo.

3.3. Effect of Contact Time

Studies were conducted at varied contact time for removal of Cadmium by pods of dalbergia sissoo from 5-120 minutes at fixed stirring speed (150 rpm), initial cadmium concentration (50 mg/l), adsorbent dose (1000 mg per 100 mL sample solution), pH (6.0) and temperature (25 ± 1^0C). The percent removal increased with time and the maximum cadmium was adsorbed within 60 min. (Fig. 2) upto the level of 99.9%.

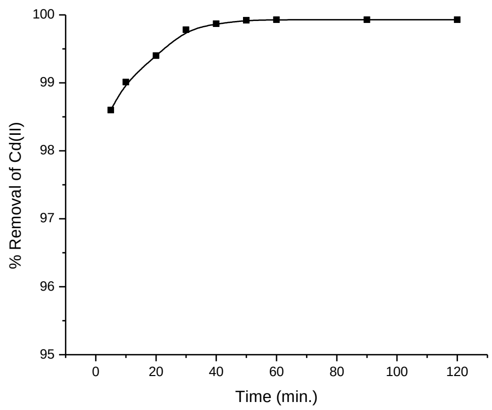


Figure 2: Effect of Contact time on % removal of Cd(II) by NaOH treated Pods of Dalbergia sissoo.

3.4. Effect of Adsorbent Dose

The percent adsorption of Cd(II) ion on pods of dalbergia sissoo was studied at different adsorbent doses (400, 800, 1000, 1200, 1400, 1600 and 2000 mg/100ml) keeping other parameters constant at cadmium concentration (50 mg/L), stirring speed (150 rpm), pH (6.0), temperature (25 ± 1^0C) and contact time (60 min.). Results showed that with increase in the adsorbent dose from 400 to 1000 mg/L, percentage adsorption of cadmium has increased from 99.82% to 99.96% . (Fig. 3). A small dose of adsorbent has proved to be such effective for removal of Cd(II) ions.

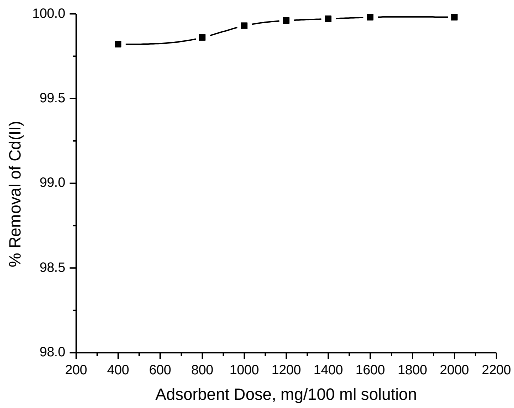


Figure.3. Effect of adsorbent dose on removal of Cd(II) by dalbergia sissoo.

3.5. Effect of Stirring Speed

The batch experiments had been performed at varied stirring speed from 50 to 250 rpm at Cd(II) conc. 50 mg/L, pH 6, temperature 25±1^{0}C, contact time 60 minutes and adsorbent dose 1000 mg/100 ml of solution. The result shows that the percent adsorption increases on increase in stirring speed from 50 to 150 rpm and thereafter it practically remains constant (Fig. 4). It may be due to the maximum dispersion of the particles of adsorbent at 150 rpm giving the maximum surface area available and thereafter no significant surface area increased.

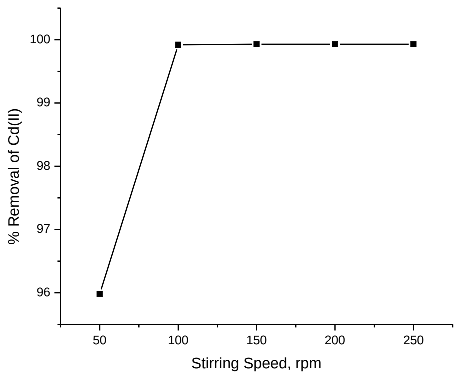


Fig. 4. Effect of Stirring Speed on removal of Cd(II) by NaOH treated pods of dalbergia sissoo.

3.6. Effect of Initial Conc. of Cd(II) ion

Effect of initial concentration of Cd(II) ion on its adsorption on pods of dalbergia sissoo was studied at its varied concentrations in solutions at 10, 20, 30, 50, 80, 100, 200, 300, 400 and 500mg/L at constant stirring speed 150 rpm, pH 6, contact time 60 minutes and adsorbent dose 1000 mg/100 mL of solution. The plot between percent adsorption vs. initial conc. of Cd(II) ion (Fig. 5) shows that the percent adsorption of Cd(II) decreases as the initial conc. of Cd(II) increases prominently after conc. 100 mg/L which may be explained that upto this conc. the surface becomes occupied by Cd(II) ions and further adsorption is restricted.

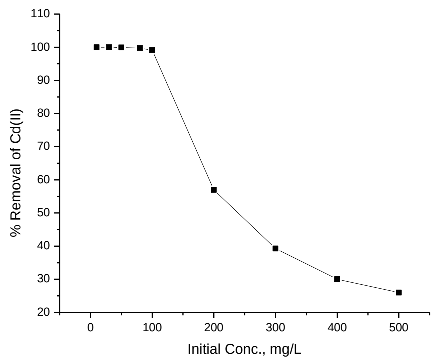


Fig. 5. Effect of initial Cd(II) ion conc. on removal of metal (Cd(II)) by NaOH treated pods of dalbergia sissoo.

3.7 Effect of Temperature

It has been observed from the Fig. 5 that the adsorption percentage increases with increase in temperature as the pore size of biomaterial and the mobility of ions increases with temperature. It also shows the endothermic behavior of the process.

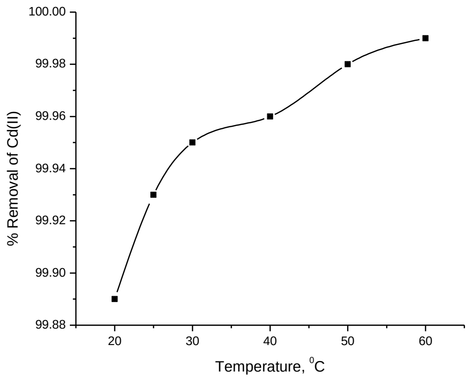


Fig. 5. Effect of temperature on removal of metal Cd(II) by NaOH treated pods of dalbergia sissoo.

3.7. Equilibrium Studies

Experimental results obtained for the adsorption of cadmium on NaOH treated pods of dalbergia sissoo at specified conditions of pH, adsorbent dose and stirring speed as 6, 1000 mg /100 mL of solution and 150 rpm respectively for 60 min. contact time and 25±1^{0}C temperature were applied to fit the Freundlich and Langmuir adsorption isotherms (TABLE 1).

Table 1. Freundlich and Langmuir Isotherms data (pH 6, Adsorbent dose 1000mg/100 mL of sample solution, stirring speed 150rpm, contact time 60 min., temperature 25±1^{0}C)

Adsorption	Freundlich Isotherm			Langmuir Isotherm		
	r^2	n	K_f	r^2	b	Q_0
Cd(II) on NaOH treated pods of dalbergia sissoo	0.99309	35.014	10.17	0.99972	1.0039	11.955

Freundlich Isotherm i.e. the linear plot of ln(x/m) versus ln C_e for various initial concentrations (Fig. 6) indicates the applicability of Freundlich isotherm to adsorption of Cd(II) on said adsorbent. The value of correlation coefficient (r^2) was found to be 0.99309 (TABLE 1) which indicates that the data fitted fairly well to Freundlich model. From the isotherm (Fig. 6), Freundlich constants K_f and n are calculated as 10.17 L g^{-1} and 35.014 respectively.

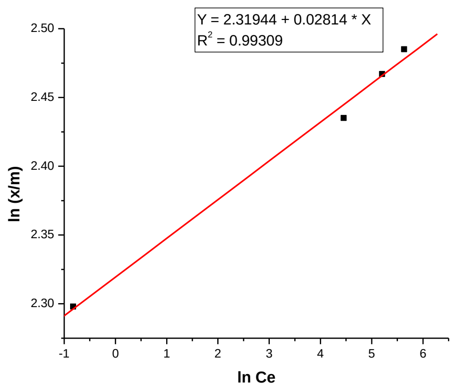


Fig. 6. Freundlich Isotherm (pH 5.5, Adsorbent dose 1500mg/100 ml of sample solution, stirring speed 200rpm, contact time 30 min., temperature 25±1^{0}C)

Applicability of Langmuir adsorption isotherm is found through the linear plot of C_e/(x/m) vs. C_e (Fig. 7). Correlation coefficient (r^2) was found as 0.99972 (TABLE 1) which indicates that the Langmuir isotherm fits quite well to the data drawn in the present studies. Slope of the isotherm has been found to be less than unity describes the significant adsorption at low concentration of Cd(II) ion. Langmuir parameters Q_0 and b are computed as 11.955 and 1.0039 respectively.

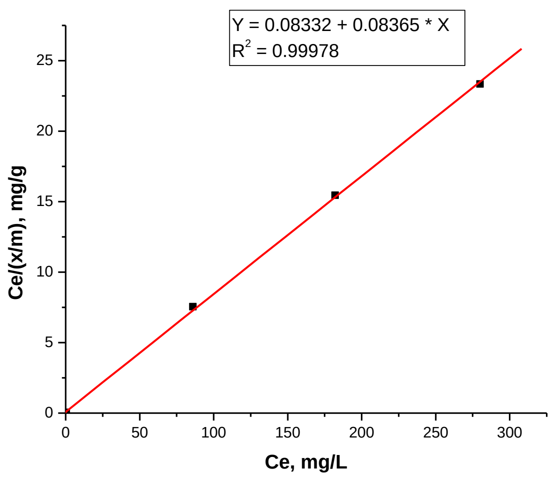


Fig. 7. Langmuir Isotherm (pH 6, Adsorbent dose 1000mg/100 mL of sample solution, stirring speed 150rpm, contact time 60 min., temperature 25±1^{0}C)

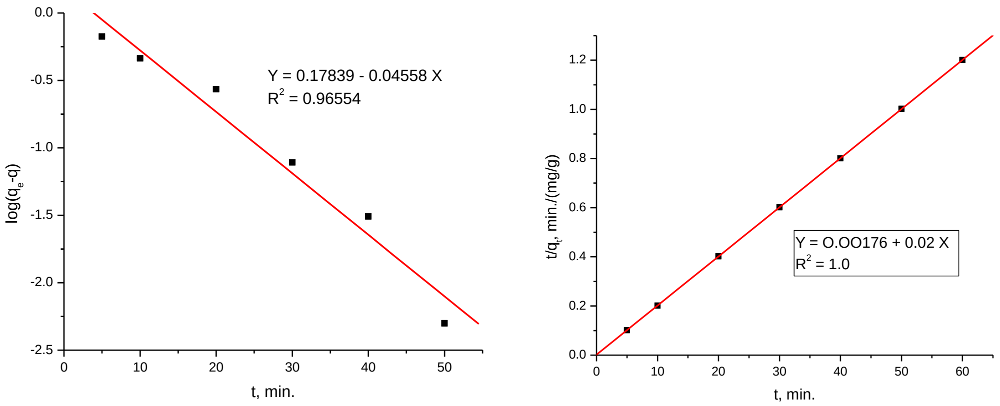
While comparing the two models for better fit to the equilibrium data, the values of r^2 show that Langmuir adsorption model fitted better as compared to Freundlich model.

3.8 Kinetic Studies

To verify first order kinetics Lagergren equation has been used. Linear plots of log (q_e-q) vs time (correlation coefficient 0.96554) which shows the applicability of above equation for first order kinetics for the adsorption of Cd(II) on NaOH treated dalbergia sissoo. The value of K_{ad} (L min^{-1}), the first order rate constant has been found to be 0.105.

The adsorption kinetics data were further analyzed using Ho and McKay's pseudo-second-order kinetic model. The slopes and intercepts of plots t/q_t versus t was used to calculate the pseudo second order rate constants k_2 and q_e (correlation coefficient 1.0) and values are 0.227 and 49.98 respectively.

From the value of correlation coefficient, it has been observed that the adsorption of Cd(II) by said biomaterial the pseudo second order kinetics.



(a) (b)

Fig. 8. (a) Lagergren First order kinetics; b) Pseudo second order kinetics

3.9 Adsorption of Cd(II) on raw pods of dalbergia sissoo for comparison with NaOH treated material

Batch experiment was performed to study the adsorption of cadmium from aqueous solutions at pH 6, initial metal ion conc. 50 mg/L, stirring speed 150 rpm, adsorbent dose 1000mg/100mL sol. for 60 minutes contact time.

The percent removal of metal ion has been found in the order of 98.4% as compared to the 99.96% in case of adsorption by NaOH treated biomaterial at similar conditions.

IV.CONCLUSION

The results show that the NaOH treated pods of dalbergia sissoo have high potential to sequester Cd(II) from aqueous solutions which can be a good alternative of commercially available adsorbents for low concentration of metal ion and high volumes of wastewater. Parameters pH, contact time, stirring speed, adsorbent dose and initial metal ion conc. affect the adsorption of Cd(II) on the said biomaterial. The adsorption is found to be maximum at pH 6, adsorbent dose as 1000 mg/100ml of sample solution, stirring speed 150 rpm and contact time 60 min. Langmuir isotherm fits quite well to explain the behaviour of adsorption of Cd(II) on NaOH treated pods of dalbergia sissoo. NaOH treatment of pods of dalbergia sissoo has shown the advantage by enhancing the capacity to remove Cd(II) ions from aqueous solutions as compared to the raw form of biomaterial. The material can effectively be used for the purpose and can be used for the industrial effluents. The results can further be used to design the flow process to sequester heavy metals from waste water streams. The study can further be enhanced for the recovery of Cd(II) metal as at very low pH the adsorption has been found to be very low which has shown the possibility of recovery of metal to avoid metal losses and to save environment.

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