An Ecofriendly Alternative for the Removal of Cd (II) and Cu (II) from Aqueous Medium

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Abstract

Different types of agricultural waste materials have been explored for their efficiency in removing heavy metal ions from aqueous solution. A biomass of Desmostachya bipinnata (DB) was investigated as the potential bio-adsorbent for the removal of Cd (II)) and Cu (II) from wastewater. The surface of DB was chemically grafted with ethylenediamine. It was characterized by elemental, FTIR and SEM analysis. The maximum adsorption capacity of MDB in the removal of Cd (II) and Cu (II) were 30.4mg/g and 41.6 mg/g at their optimum pH 6 and 5, respectively. The experimental data followed the Langmuir isotherm and pseudo-second order kinetic model The research results indicated that D. bipinnata can be an alternative, efficient and ecofriendly material for the removal of Cd (II) and Cu (II) from wastewater.

Keywords: *Desmostachya bipinnata, Biosorption, Heavy metals, Batch experiment, Pseudo-second order kinetic model, Ecofriendly.*

Introduction

Water pollution caused by heavy metals is a matter of great environmental concern. The common toxic heavy metals found in industrial wastewater are Pb, Cd, Cr, Ni, Mn, Hg, Cu and Zn[1, 2]. Appreciable concentration of these metal ions in water supplies exceeding the standard, constitutes a sever health hazard. Their harmful effects in aquatic environment include accumulation in living species and magnification throughout the food chain[3]. Cd (II) is one of the most toxic metal which is exposed to environment from welding, electroplating, pesticide fertilizer and Cd-Ni battery which can cause kidney damage, gastrointestinal disorder, bone marrow cancer and bronchitis[4, 5]. Although Cu is an essential metal, extensive intake leads to sever mucosal irritation, hepatic and renal damage, hemolytic and heart failure and muscleache[6].

Under such circumstances, these metal ions should be removed prior to their discharge into environment. The presently existing techniques for the removal of low concentration of heavy metals from wastewater include membrane separation, ion exchange and adsorption. Recently many researchers have given attention for the investigation of new adsorbent materials which are cost effective, efficient as well as eco-friendly. In this regard, agricultural waste, different types of algae, seaweeds, sunflower stalks, fruit peels, and tea waste are used. They are renewable, easily available in the local level with low cost[7, 8]. The present study explores the possibility to introduce amine functional group into cellulose network contained in DB, for the effective removal of heavy metals from aqueous solution.

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Experimental Methods

Sample preparation

The plants of *Desmostachya bipinnata* were dried, cut and ground in to fine powder This sample is referred to as raw *Desmostachya bipinnata* (RDB) which was chemically modified with ethylenediamine after acid treatment for better adsorption of metal ions. Thus prepared biosorbent is known as modified *Desmostachya bipinnata* (MDB).

1000 mg/L of standard stock solution of Cadmium (II)) and Copper (II) metal ions were prepared from analytical grade of Cadmium nitrate and Copper sulphate using milli-Q deionized water. All the working solutions of various concentrations (25, 50, 100, 200, 400, 600 and 800 mg/L) were prepared by diluting the standard stock solution with 0.1 M nitric acid and 0.1 M 2-[4-(hydroxymethyl)-1-piperazinyl] ethanesulphonic acid (HEPES) was used as buffering agent in all working solutions[9].

Effect of pH

The effect of pH onto Cd (II) and Cu (II) metal ions were analyzed over the pH range from one to seven. 50 mg/L of metal solution was taken in a beaker and pH was adjusted by adding dilute nitric acid and sodium hydroxide solution as required, with constant stirring. 20 ml of Cd (II) metal solution at pH-1 was taken in two separate conical flasks and 25 mg of biosorbent (MDB) was added in only one conical flask covered the mouth with paraffin paper and shaken in a shaker at 23 ^{0}C for 24 h at 150 rpm. The next flask with 20 ml of metal solution was taken as the reference. After 24 h, it was filtered through cellulose free filter paper and pH was analyzed using pH-meter and concentration of the metal ion was monitored using ICP-AES. The same process was repeated for all the respective metal ions at all pH from one to seven.

Effect of Metal ions concentration

Working solutions of 25, 50, 100, 200, 400, 600 and 800 mg/L were prepared by diluting the standard stock solution with 0.1 M nitric acid and 0.1 M HEPES as the buffering agent. 20 ml of metal solution of various concentrations were taken at their optimum pH (6 and 5 for Cd (II) and Cu (II), respectively) in conical flasks separately then 25 mg of biosorbent (MDB) was added in each flask, covered the mouth with paraffin paper and shaken in a shaker at 23^0 C at 150 rpm for 24 h. Reference solution of each concentration was kept for analysis. After 24 h of shaking, the solutions were filtered and the residual metal ions concentrations were measured using ICP-AES. The results obtained were analyzed using Langmuir Isotherm for each metal ions. References of each metal ions were run to detect any metal precipitation. From the metal ion concentration measured before and after the adsorption (C_i mg/L and C_e mg/L) and dry weight of adsorbent (W, gm), as well as volume of aqueous metal ions solution (V, ml), the amount of adsorption of metal ions (q, mg/g) was calculated according to equation (1) .The adsorption percentage (A%) defined as the ratio of the decrease in metal ion concentration in aqueous solution before and after the adsorption (C_i-C_e) to its initial concentration (C_i) was calculated according to equation (2)

$$q = \frac{C_i - C_e}{W} \text{ X V} \qquad\qquad (1)$$

$$A \% = \frac{C_i - C_e}{C_i} \text{ X } 100 \qquad\qquad (2)$$

Effect of contact time

The effect of contact time of the metal ions onto MDB was analyzed as the function of time at an initial concentration of 50 mg/L solution. In this study 20 ml of metal ions solution were taken in 14 different conical flasks and 25 mg of biosorbent was added in each flask covered with paraffin paper and shaken at 23 ^{0}C at 150 rpm for different interval of time ranging from 5 minutes to 360 minutes. After the completion of each shaking time the solution was filtered and corresponding concentrations were measured using ICP-AES (SPECTRO, Analytical Instruments, Kleve, German).

Results and Discussion

The amount of carbon and nitrogen was found to be 41.27% and 1.13% in raw *Desmostachya bipinnata* (DB). After chemical modification, percentage of nitrogen was found to be 5.49%. Increase in nitrogen percentage shows the introduction of amino group in the biosorbent.

(1a)

(1b)
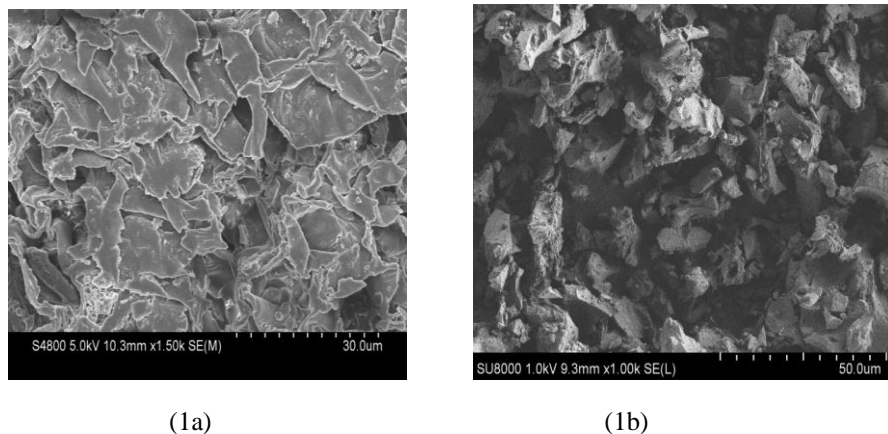
*Figure 1: Scanning electron microscope (SEM) photographs of (1a) RDB and (1b) MDB*

Surface morphology of DB was studied with scanning electron microscope (SEM) before and after chemical modification. The morphological difference on the surfaces of RDB and MDB can be visualized in figure 1a and 1b[8].It is found that the surface of the MDB became much rough with porous structure than that of the RDB, after surface modification reaction. The introduction of the amino group on the surface of the biosorbent can therefore be expected to change the material's properties and thus affects the metal ion adsorption.

FTIR spectra have been a useful tool in identifying the presence of certain functional groups in a molecule[10]. To confirm the types of functional groups on the biosorbent before and after chemical modification, FTIR spectra of RDB and MDB were determined and are shown in figure 2. The characteristic peaks in the spectrum of RDB can be assigned as follows. 3409 cm^{-1}(OH stretching), 2926 cm^{-1}(CH stretching in CH$_2$ and CH$_3$ groups), 1736cm^{-1} (C=O stretching), 1426-1369 cm^{-1} (O-H bonding), 1169-1083 cm^{-1} (C-O stretching vibration of alcohol) [11,12]. After the chemical modification of biosorbent, the spectrum of MDB shows some significant changes in figure 2. The intense sharp peak at 3409 cm^{-1} in RDB has been shifted to 3393 cm^{-1} as a broad peak in MDB, which suggest the overlapping of hydroxyl groups with amine groups in MDB. Similarly peak at 1639 -1588 cm^{-1} in RDB are overlapped as a broad peak in MDB, indicates the amine group introduction onto the surface of chemically modified biosorbent. Some of the peaks of RDB at 2926cm^{-1}, 1124 cm^{-1}, 1169 cm^{-1}, are significantly reduced in MDB, where as some peaks at 1736 cm^{-1}, 1466 cm^{-1}, 1245 cm^{-1}, 883 cm^{-1} are lost.
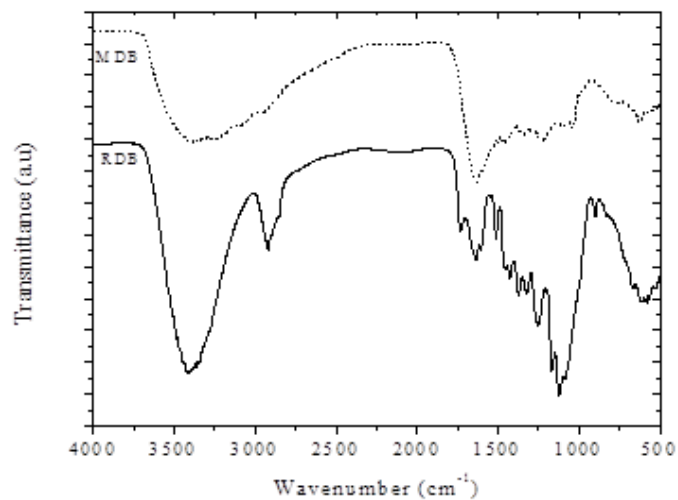
Figure 2: *FTIR of (a) RDB and (b) MDB*

The efficiency of metal ions removal by MDB was affected by the initial pH of the Cd (II) and Cu (II) metal ions solution. The adsorption of respective metal ions onto MDB showed that the removal efficiency increased with the increase in pH of the metal ions solutions till pH of around 5- 6. At low solution pH, large quantity of protons (H^+) existed which is greater as compared to metal ions and the competitions between H^+ with metal ions decreases their removal efficiency. Further metal ions removal above the optimal pH condition decreases owing to the excess hydroxyl ions at this region as well due to their precipitating nature. The result of the pH study showed that maximum removal efficiency obtained were at pH 6and 5 for Cd (II) and Cu (II), respectively as shown in fig. 3.
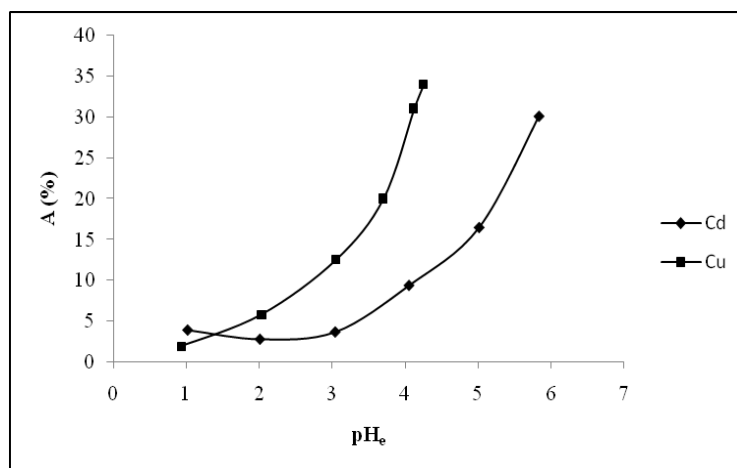
Figure 3: *Effect of pH in the adsorption of Cd (II) and Cu (II) onto Modified Desmostachya bipinnata*

The effect of initial concentration of Cd (II) and Cu (II) ions removal were studied at 25 to 800 mg/L of metal ions at fixed adsorbent dose of 25 mg at their optimum pH as shown in fig 4. The adsorption isotherms were evaluated with the help of linearzed Langmuir model represented by equation (3).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (3)$$

Where q_e (mg/g) is the amount of adsorbed metal ions per gm of adsorbent, C_e (mg/L) is the residual concentration of metal ions after adsorption, q_m (mg/g) is the maximum adsorption capacity and b(L/mg) is the binding constant. The Langmuir constant (q_m and b) were calculated from plots of C_e/q_e versus C_e. The Langmuir parameters are given in table 1.

**Table1:** *Langmuir adsorption isotherm model parameters and experimental q_{max}*

Metal ions	Langmuir q_{max} (mg/g)	Experimental q_{max} (mg/g)	b (L/mg)	R^2
Cd (II)	34.48	30.40	0.012	0.998
Cu (II)	45.45	41.60	0.014	0.995
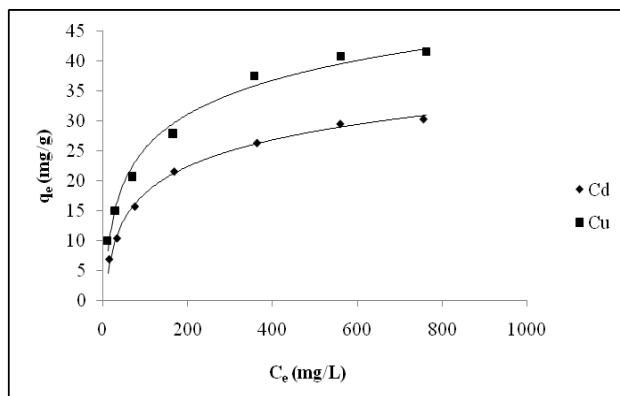
Figure 4: *Adsorption isotherm for the Cd (II) and Cu (II) onto Modified Desmostachya bipinnata*

Based on the correlation coefficient (R^2) value, the adsorption isotherms for the Cd (II) and Cu (II) were well described by the Langmuir equation. The maximum adsorption values (q_m) were 30.4 mg/g and 41.6 mg/g for Cd (II) and Cu (II), respectively. On the other hand, theoretical monolayer capacity (q_m) of the respective metal ions based on the Langmuir adsorption equation as shown in fig. 5, were determined to be 34.48 mg/g and 45.45 mg/g, respectively, which are in close agreement with the experimental (q_m) results suggesting that heavy metals can be quantitatively removed by the (MDB) biosorbent.

The effect of contact time on the removal of Cd (II) and Cu (II) metal ions from aqueous solution by biosorbent were studied using pseudo-second order kinetic models as shown in fig. 6. The kinetic plots of t/q_t (min/mg/g) versus t (min) gave the straight line for the respective metal ions onto the MDB as shown in fig. 7, indicating that adsorption reaction can be approximated with pseudo-second order kinetic model given by Ho and McKay[13].
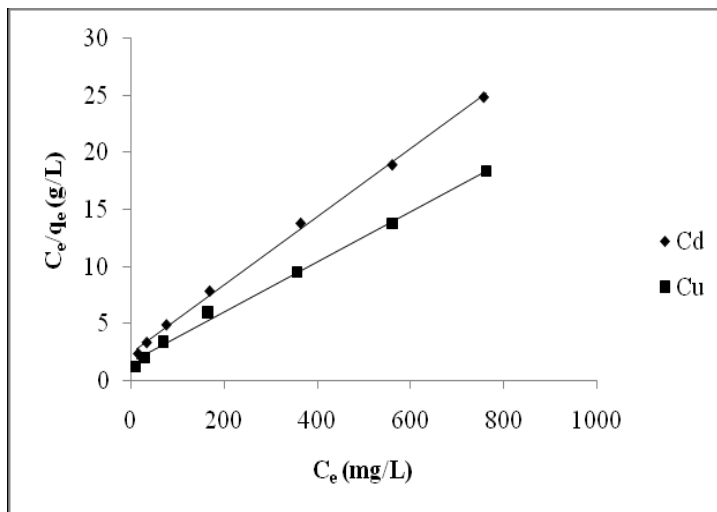
Figure 5: Langmuir plot for the adsorption of Cd (II) and Cu (II) onto Modified Desmostachya bipinnata

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Where q_t (mg/g) is the amount of adsorption at time t (min), K_2 (g/mg/min) is the rate constant of the pseudo- second order kinetic adsorption. Value of K_2 and q_e can be obtained from the intercept and slope of the of experimental t/q_t versus t, which is given in table 2.
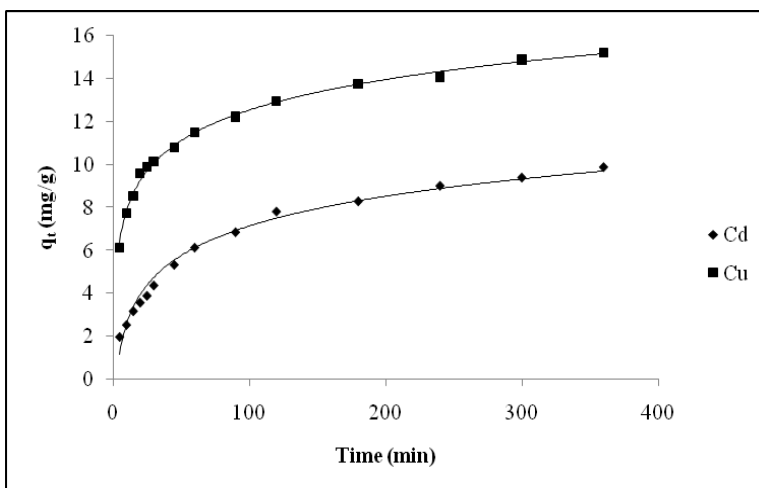
Figure 6: Adsorption kinetics of Cd (II) and Cu (II) onto Modified Desmostachya bipinnata

Table2: Sorption kinetics of pseudo second order for Metal ions onto MDB

Metal ions	R^2	K_2(g/mg/min)
Cd (II)	0.997	2.339×10^{-3}
Cu (II)	0.995	3.824×10^{-3}
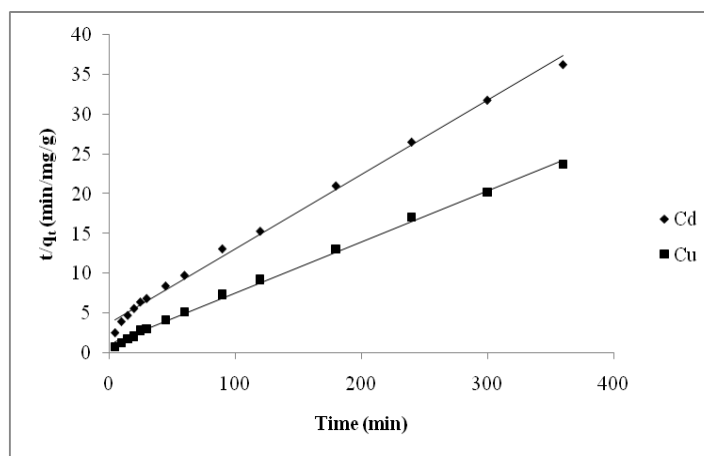
Figure 7: Pseudo second- order kinetic model in the adsorption of Cd (II) and Cu (II) onto Modified Desmostachya bipinnata

The result showed that the adsorption increased with the increase in time from 5 minutes to 100 minutes and then it became almost constant. So the best contact time was considered at 90 to 100 minutes. The correlation coefficient for the second order kinetic model is greater than 0.99, which indicated that the adsorption model followed the pseudo second-order kinetic model.

Conclusions

This research work has introduced a new adsorbent *Desmostachya bipinnata* (DB) which is available at local level at almost free of cost**.** Elemental analysis, SEM and FTIR analysis revealed the introduction of amine group onto the DB. Equilibrium isotherms and kinetic studies performed by batch adsorption experiments at their optimum pH indicated that DB has reasonable maximum adsorption capacities for Cd (II) and Cu (II) metal ions, respectively. The adsorption process followed the pseudo second order kinetics. Based on the properties and maximum loading capacity for the tested metal ions, the chemically modified DB can be an ecofriendly and cost effective alternative for the removal of heavy metal ions from aqueous solution. However further studies concerning recovery of heavy metals experiment and reuse of biosorbent should be carried out to investigate the potential of MDB and improve the adsorption process.

Acknowledgements

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