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Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon

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ABSTRACT: The effective removal of heavy metals from industrial wastewater is among the most important issues for many industrialized countries. Removal of lead(II) and cadmium(II) from aqueous solutions were studied using *Tridax procumbens* (Asteraceae). Batch adsorption experiments were performed as a function of pH, contact time, solute concentration and adsorbent dose. The optimum pH required for maximum adsorption was found to be 4.5 and 4.8 for lead and cadmium, respectively. The maximum contact time for the equilibrium condition is 180 min at the sorbent dose rate of 2.5 g. The maximum efficiencies of lead and cadmium removal by biocarbon were 95% and 98%, respectively. The results were well fitted by both Langmuir and Freundlich isotherm models.

KEYWORDS: heavy metals, water treatment, biosorption, biomaterials, *Tridax procumbens*

INTRODUCTION

The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life. They accumulate in living tissues throughout the food chain which has humans at its top. These toxic metals can cause accumulative poisoning, cancer, and brain damage when found above the tolerance levels[1]. Lead compounds are very toxic to humans. The presence of lead in drinking water above the permissible limit (5 ng/ml) may cause adverse health effects such as anaemia, encephalopathy, hepatitis, and nephritic syndrome[2]. Hence it is very important that lead should be removed from wastewater before being discharged into an aquatic environment.

Several conventional methods exist for the removal of heavy metal pollutants from wastewater. These methods include precipitation, electroplating, chemical coagulation, ion-exchange, membrane separation, and electrokinetics. However, these methods often incur high operational costs[3–5].

Biosorption of heavy metals from aqueous solution is an efficient technology in industrial wastewater treatment. A number of studies have demonstrated the feasibility of using plant biomass[6–8] and also using biomass of micro-organisms[9–11] to remove heavy metal ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. Biosorption processes are particularly suitable for the treatment of wastewater containing low concentrations of heavy metals[12].

In this study an attempt was made to determine the effectiveness of the activated biocarbon derived from a traditional medicinal plant, *Tridax procumbens* (Asteraceae) which is widely distributed in agricultural fields. It was used to remove cadmium and lead from synthetic wastewater and to investigate the mechanisms of adsorption onto activated biocarbon by performing a batch experimental process. The present investigation was aimed to study the effects of pH, contact time, initial concentration, and biocarbon loading for the removal of lead and cadmium ions from wastewater using the activated biocarbon.

MATERIALS AND METHODS

Preparation of synthetic wastewater

Synthetic wastewater samples were prepared by using analytical grade lead nitrate and cadmium chloride. For pH adjustment throughout the experiment, hydrochloric acid and/or sodium hydroxide solutions were used as necessary. The stock solutions contained 100 mg/l of Pb(II) and Cd(II), respectively.

Biocarbon preparation

Tridax procumbens plant leaves were collected and air dried for 48 h. The dried leaves were grounded in ball mills and the screened homogeneous powder was used for the preparation of biocarbon. Activated biocarbon of the *T. procumbens* was prepared by treating the leaves powder with the concentrated sulphuric acid (SG 1.84) in a weight ratio of 1:1.8 (biomaterial:acid). The resulting black product was kept in an air-free oven maintained at $160 \pm 5\,°C$ for 6 h followed by washing with distilled water until free of excess acid, and then dried at $105 \pm 5\,°C$. The particle size of activated carbon between 90 and 125 µm was used. Batch experiments were performed at $27 \pm 2\,°C$. The samples were mechanically agitated at 100 rpm. The concentrations of lead and cadmium were estimated using Shimadzu AA 6200 with an acetylene-air flame system[13].

The proportion of heavy metal removed from solution was calculated from $(C_0 - C_e)/C_0$ where C_0 and C_e are, respectively, the initial and final concentrations of heavy metal. The amount of adsorbed metal ions per unit mass of biocarbon was obtained from $q_e = (C_0 - C_e)V/m$, where V is the volume of the medium, and m is the mass of biocarbon used.

RESULTS AND DISCUSSION

Effect of pH

The pH is one of the most important parameters of biosorption of heavy metals[14]. The biosorption of lead and cadmium by activated biocarbon of *T. procumbens* at different pH values is presented in Fig. 1. In the present investigation, the rate of removal of Pb(II) and Cd(II) ions in synthetic wastewater is mainly controlled by pH of the solution. The optimal pH for Pb(II) and Cd(II) removal was 4.5 and 4.8, respectively. At pH higher than 6 both metals were precipitated due to the formation of hydroxides and removal due to sorption was very low. At low pH the concentration of protons was high and metal binding sites became positively charged repelling the Pb(II) and Cd(II) cations. With an increase in pH, the negative charge density on the biocarbon increases due to deprotonation of the metal binding sites, thus increasing metal biosorption. Similar results were found with tree fern where it has been shown that pH values in the range of 4.0 to 7.0 are adequate for lead binding, of which pH 4.9 is the optimum value for the biosorbent[15].

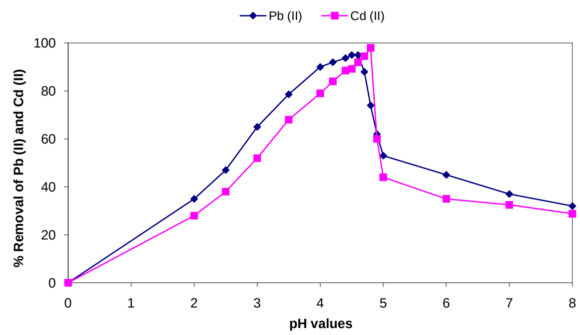

Fig. 1 Effect of pH on the removal of Pb(II) and Cd(II) ions.

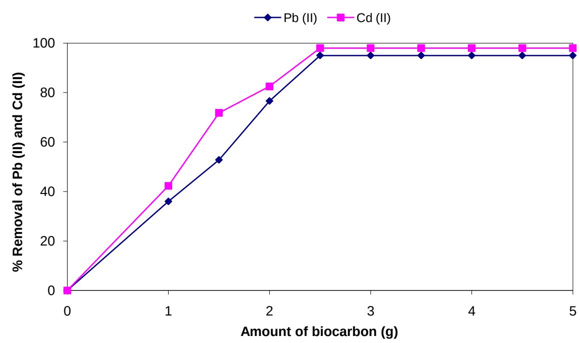

Fig. 2 Effect of amount of biocarbon on the removal of Pb(II) and Cd(II) ions.

Effect of amount of biocarbon

It is important to fix the amount of the activated biocarbon of the biosorbent to design the optimum treatment systems and for a quick response of the analysis. To achieve this aim, a series of batch experiments were conducted with the adsorbent dose of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 g per 100 ml of test solution. When the addition of the adsorbent dose increased, the percentage removal of metal ions also increased. A maximum removal of 95% of lead and 98% of cadmium, respectively, was obtained at 2.5 g of the activated biocarbon. It can be seen from Fig. 2 that an adsorbent dose of 2.5 g is sufficient for optimal removal of both metals in aqueous solutions. A further increase in the quantity of biocarbon dose will not have any significant effect on the removal of lead and cadmium ions from the solution. Potgieter et al[16] reported similar findings for heavy metal removal from aqueous solutions by using palygorskite clay as an adsorbent.

Effect of contact time

After optimization of the bioadsorbent dose at 2.5 g per 100 ml test solution and the pH at 4.5 for lead ion solution and 4.8 for cadmium ion solution, the effect of contact time for the efficient removal of metal ions was studied. The two metals showed a steady rate increase of sorption during the sorbate-sorbent contact process and the rate of removal became al-

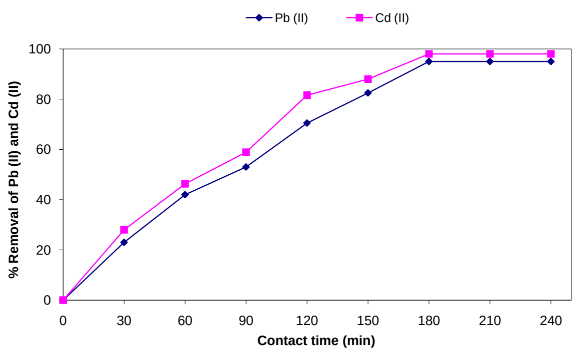

Fig. 3 Effect of contact time on the removal of Pb(II) and Cd(II) ions. $C_0 = 100$ mg/l. Biocarbon dose = 2.5 g.

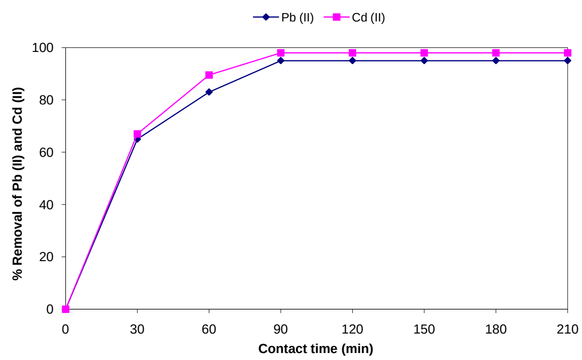

Fig. 4 Effect of concentration of metal ions on the removal of Pb(II) and Cd(II) ions. $C_0 = 50$ mg/l. Biocarbon dose = 2.5 g.

most insignificant due to a quick exhaustion of the adsorption sites. The rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals [17]. In these studies, 95% removal of lead and 98% removal of cadmium were achieved at 180 min. Further, no significant changes were observed in the removal of both metal ions from the solution after 24 h of equilibration (Fig. 3).

Effect of metal ions concentration

The metal uptake mechanism is particularly dependent on the heavy metal concentration. Initial concentrations of 50 and 100 mg/l of metal ions were selected for the comparative study for the removal of Pb(II) and Cd(II). Fig. 4 shows the effect of metal concentration on the removal of lead and cadmium ions. At the metal ion concentration of 50 mg/l and the optimum dose of 2.5 g of the activated biocarbon the maximum removal of Pb(II) and Cd(II) was achieved within 90 min. However, at 100 mg/l, the maximum removal was only after 180 min. This observation clearly indicates that the removal of metal ions purely depends on the amounts of adsorbent and contact time. The heavy metals are adsorbed by specific sites provided by the acidic functional groups on the biocarbon, while with increasing metal concentrations the specific sites are saturated and the exchange sites due to excessive surface area of the biocarbon are filled [18]. It is clear that with increasing initial concentrations, the metal removal decreases.

Biosorption isotherms

The adsorption isotherms are very important in describing the adsorption behaviour of solutes on the specific adsorbents. In this work, two important isotherm models such as Langmuir and Freundlich were selected and studied. The Langmuir isotherm takes an assumption that the sorption occurs at specific homogeneous sites within the biosorbent [19]. A general form of the Langmuir equation is

$$q_\mathrm{e} = \frac{b\, q_\mathrm{max} C_\mathrm{e}}{1 + b\, C_\mathrm{e}}. \tag{1}$$

The linear form of isotherm equation can be written as

$$\frac{1}{q_\mathrm{e}} = \left(\frac{1}{b\, q_\mathrm{max}}\right)\left(\frac{1}{C_\mathrm{e}}\right) + \left(\frac{1}{q_\mathrm{max}}\right),$$

where q_max is the maximum metal uptake corresponding to the saturation capacity of the biosorbent and b is the energy of biosorption. The variables q_e and C_e are, respectively, the amount of metal adsorbed on the biocarbon and the equilibrium metal concentration in solution. The constants q_max and b are the characteristics of the Langmuir isotherm and can be determined from (1). Therefore a plot of $1/q_\mathrm{e}$ versus $1/C_\mathrm{e}$ gives a straight line of slope $(1/b\, q_\mathrm{max})$ and intercept $(1/q_\mathrm{max})$. The data fit the Langmuir isotherms model well for Pb(II) and Cd(II) ions (Figs. 5,6).

The values of Langmuir and Freundlich parameters for the removal of both Pb(II) and Cd(II) metals ions are presented in Table 1. The correlation coefficient (r^2) for the biosorption of Pb(II) and Cd(II) are 0.958 and 0.9862, respectively. The linearity of the two plots (Fig. 5b and Fig. 6b) indicates application of the Langmuir equation, supporting monolayer formation on the surface of the biosorption. The values of b and q_max indicate that the biosorption of the metal ions are concentration and pH dependent.

The expression of separation factor (R_L) in the dimensionless form of the Langmuir isotherm is $R_\mathrm{L} = 1/(1 + b\, C_0)$, where C_0 is the initial concentration of metal ion and b is the Langmuir constant. The

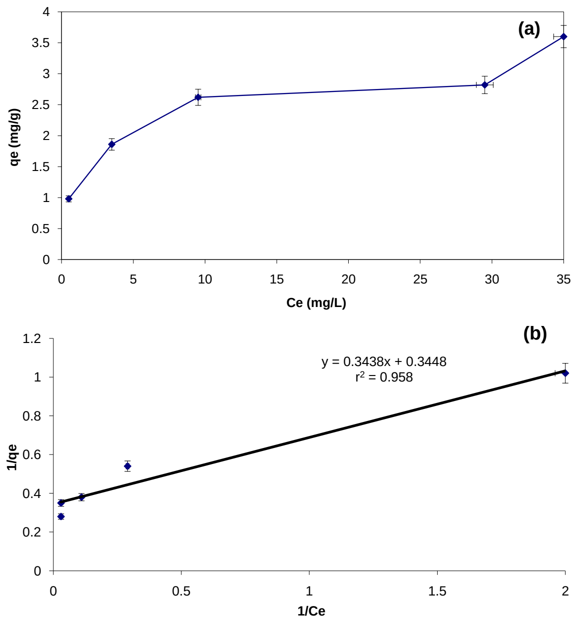

Fig. 5 (a) Biosorption isotherm and (b) Langmuir isotherm for Pb(II) ions removal on activated biocarbon.

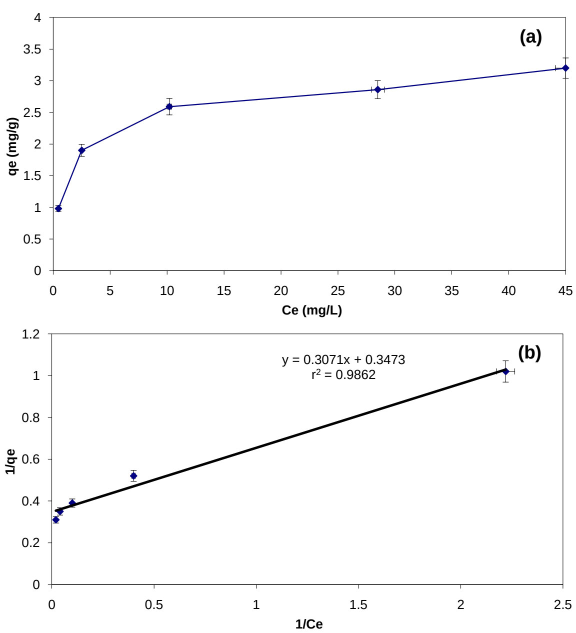

Fig. 6 (a) Biosorption isotherm and (b) Langmuir isotherm for Cd(II) ions removal on activated biocarbon.

separation factor (R_L) can be used to predict affinity between the sorbate and sorbent in the biosorption system[20]. The characteristics of the R_L value indicates the nature of biosorption as unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), and irreversible ($R_L = 0$). It is well observed that, in all selected concentrations (25–125 mg/l) of metal ions, the separation factor (R_L) is less than 1.0 indicating the favourable biosorption conditions.

Table 1 Langmuir constants and correlation coefficient for biosorption of Pb(II) and Cd(II) ions on activated biocarbon.

Metal ions	Langmuir parameters		
	q_{max} (mg/g)	b (l/mg)	r^2
Pb(II)	2.90	1.00	0.9580
Cd(II)	2.88	1.13	0.9862
	Freundlich parameters		
	K_f [(mg/g) (mg/l)^n]	n	r^2
Pb(II)	1.2511	3.53	0.9626
Cd(II)	1.3286	4.06	0.9504

The Freundlich expression is an empirical equation based on a heterogeneous surface. The general form of Freundlich equation is

$$q_e = K_f \, C_e^{1/n}$$

and the linearized form of this model is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e,$$

where the intercept $\log K_f$ is a measure of biosorption capacity, and the slope $1/n$ is the intensity of biosorption. The variables q_e and C_e are the amount of metal ion adsorbed and the equilibrium metal ion concentration in solution. The Freundlich biosorption models are presented in Fig. 7. It is also observed that the Freundlich isotherm model is well fitted for the two metal ions.

Biosorption kinetics

The kinetics of the biosorption of Pb(II) and Cd(II) ions was studied using the Lagergren kinetic model. The biosorption data presented in Fig. 3 were fitted with the following pseudo-first-order rate equation:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t,$$

where q_e and q_t refer to the amount of metal ions adsorbed per unit weight of biocarbon at equilibrium and at any time t. The plots of $\log(q_e - q_t)$ versus t were straight lines. The correlation coefficients (r^2) for the removal of Pb(II) and Cd(II) ion were 0.9564 and 0.9579, respectively. The pseudo-first-order rate constant (k_1) calculated from the slopes of these plots was found to be 0.0129 min^{-1} and 0.0152 min^{-1} for the initial concentration of 100 mg/l of the metal ions.

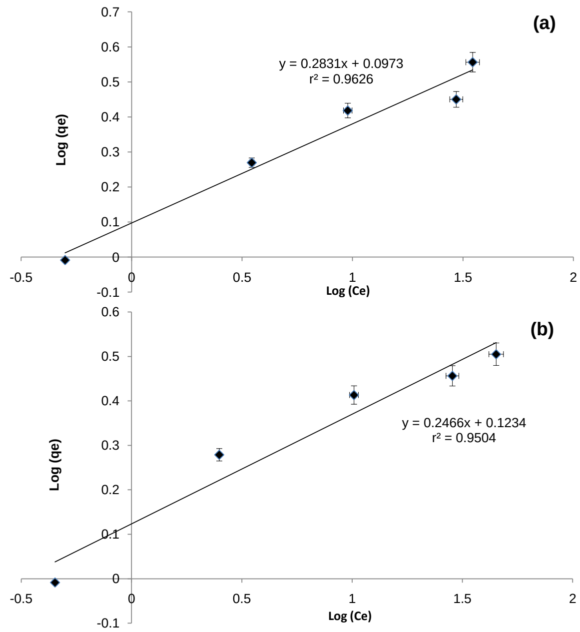

Fig. 7 Freundlich isotherm for (a) Pb(II) and (b) Cd(II) biosorption.

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