



Removal of Cd(II) by adsorption on agricultural waste biomass

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ABSTRACT

The adsorption of Cd(II) from aqueous solution using Canola biomass was investigated in a batch system. The effect of various factors such as contact time, initial concentration of Cd(II), amount of adsorbent and size of adsorbent particles of solution on the adsorption capacity of Canola biomass was determined. The equilibrium contact time was obtained to be 75 minutes indicating fast adsorption. The adsorption of Cd(II) on Canola biomass was observed to increase from 3.24 to 25.16 mg/g with increase in initial Cd(II) concentration from 10 to 100 mg/L. Kinetic and isotherm studies indicate that the adsorption of Cd(II) was best described by the pseudo-second order kinetic equation and Langmuir isotherm equations respectively. Results obtained indicate that Canola biomass can be used as an efficient adsorbent for the removal of Cd(II) from aqueous solution.

Keywords: Cd(II), Canola biomass, adsorption capacity, Kinetics, isotherms

INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. The metals are of special concern because they are non-degradable and therefore persistent. The removal of toxic heavy metals ions from sewage, industrial and mining waste effluents has been widely studied in recent years. Their presence in streams and lakes has been responsible for several health problems with animals, plants, and human beings. One of the most important toxic metals, cadmium finds its way to the water bodies through wastewaters from metal plating industries and industries of cadmium nickel batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys.

Chemical precipitation is the most common conventional method of treatment for cadmium containing effluents but large amount of sludge produced during the treatment poses disposal problems[1,2]. Ion exchange, vacuum evaporation, solvent extraction, membrane technologies, etc[3,4]. are the other well known methods employed for treatment of cadmium containing wastewaters[5,6]. Precipitation methods are particularly reliable but require large settling tanks for the precipitation of voluminous alkaline sludges and a subsequent treatment is needed[7,8]. Ion-exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated[9,10]. This has encouraged research into discovering materials that are both efficient and cheap[11,12].

Adsorption is an alternative technique for heavy metal removal[13]. The activated carbon is the most widely used adsorbent material[14]. In fact, use of activated carbon can be expensive for regeneration required and at loss of the

application processes[15,16]. Many researchers have been investigating new adsorbent materials for alternative to activated carbon, such as seaweed, marine algae, clays, activated sludge biomass, perlite, maple sawdust, etc. for the removal of heavy metal from wastewater[17,18].

Canola stalk is one of lignocellulosic wastes that are widely produced in Iran and all of the world due to the growth of the production and consumption of vegetable oils; therefore, the Canola stalk is easily available and due to its characteristics has been used in several studies to remove the pollutants[19-22].

MATERIALS AND METHODS

Cadmium(II) solution was prepared from a reagent grade cadmium(II) nitrate salt to meet the concentration 4.45 mmol/L (500 mg/L) as a stock solution. The solution was diluted by deionized water to obtain desired solution for adsorption experiments.

Adsorbent

The Canola waste used as adsorbent in this study was obtained of Tabriz agricultural school. The Canola waste was first cut into small pieces, was extensively washed with tap water to remove adhering dirt and soluble components such as tannins, resins, reducing sugar and colouring agents, and then was oven-dried at 50–60 °C until constant weight. The prepared biomass was then treated with 0.5 M H₂SO₄ for 2 h followed by the washing with distilled water and subsequently was oven dried at 105°C for 5 h. The washed and dried material was crushed and sieved to obtain a particle size lower than 1.5 mm.

Adsorption experiments

Batch experiments were carried out at various particle size (10–100 mesh), adsorbent dose (0.5–5 g/L), for a contact time of 60 min. For each batch experiment, 100 ml Cd(II) solution of 50 mg/L concentration was used. After setting pH, desired amount of adsorbent was added and the mixture was agitated on mechanical shaker for 60 min. After that the mixture was centrifuged at 4000 rpm for 10 min to separate the adsorbent from supernatant. The biosolids were then removed by filtration through glass fibre prefilters (Milipore AP40) and the filtrates were analysed for residual cadmium concentration by atomic adsorption spectrophotometry (Perkin-Elmer model AA300) with an air-acetylene flame. Cadmium hollow cathode lamp was used.

All experiments were replicated thrice for all the adsorbents and results were averaged. The removal percentage (R%) of cadmium was calculated for each run by following expression[23,24]:

$$R = \frac{(C_0 - C_e) \times 100}{C_0}$$

where C_0 and C_e were the initial and final concentration of cadmium in the solution. The adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbate in a system with solution volume V is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of cadmium (II) ions at equilibrium were calculated by[25,26]:

$$q_e = \frac{(C_0 - C_e) \times V}{M}$$

RESULTS AND DISCUSSION

Effect of adsorbent dose and particle size: The removal of Cd(II) with Canola biomass was studied at different dose (0.5–5 g/L) with keeping Cd(II) concentration (50 mg/L), stirring speed (200 rpm), pH (7.0) and contact time (75 min) constant. The results (Fig. 1) indicate that increase in adsorbent dose resulted in a higher removal of Cd(II). Maximum removal was observed at adsorbent dose of 3 g/L. The increase in the percentage removal with increase in the adsorbent dosage is due to the increase in the number of adsorption sites[27-29]. The adsorption capacity was lesser at higher adsorbent doses (Fig. 1). This may be attributed to overlapping or aggregation of adsorption sites resulting in decrease in total adsorbent surface area available to metal ions and an increase in diffusion path length[30,31].

Fig. 2 shows the effect of particle size on the adsorption of Cd(II) by Canola biomass. It is seen that the removal of Cd(II) increases as the particle size diameter decreases. Decrease in particle size increases the percentage removal due to increase in surface area as well as micro pore volume[32,33].

Effect of Initial Concentration and Contact Time

The effect of initial Cd(II) concentration and contact time on the adsorption of Cd(II) is shown in Fig. 3. It could be seen that the amount of Cd(II) adsorbed per unit mass of adsorbent increased with the increase in initial concentration and contact time until equilibrium was reached at about 75 min. However, the percent Cd(II) removal decreased with the increase in initial concentration. Fig. 3 also shows rapid adsorption of Cd(II) in the first 45 min for all initial concentrations, and thereafter the adsorption rates decreased gradually till it reached equilibrium. The higher rate of adsorption at the beginning was due to large available surface area of the biosorbent and after the capacity of the biosorbent gets exhausted (i.e. at equilibrium), the rate of uptake is controlled by the rate at which the sorbate is transported from the exterior to the interior sites of the biosorbent particles[34-36].

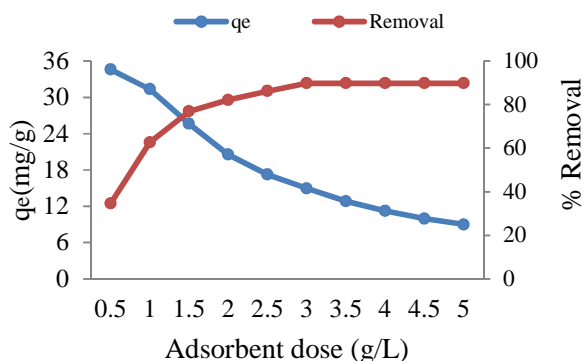


Fig.1. Effect of adsorbent dose ($C_0 = 50$ mg/L, pH=7, Contact time=75 min, adsorbent size =100 mesh)

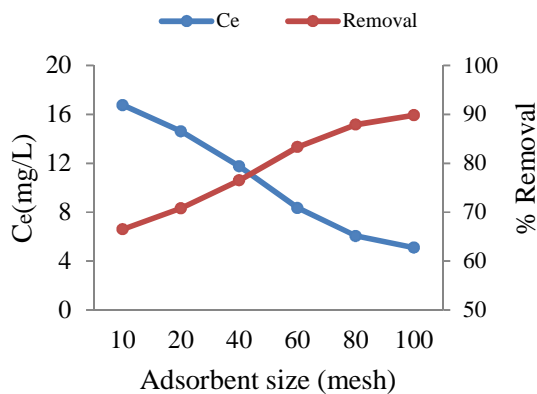


Fig 2. Effect of particle size ($C_0 = 50$ mg/L, pH=7, Contact time=75 min and dose= 3 g/L)

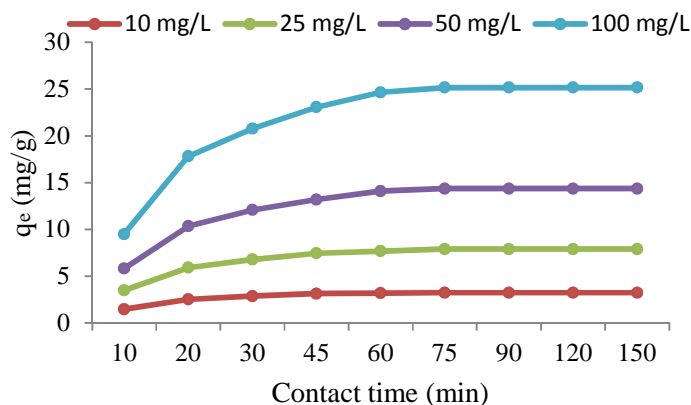


Fig 3. Effect of contact time and Initial Concentration on adsorption capacity (pH =7, dose =3 g/L and particle size=100 mesh)

Adsorption Isotherm

Two sorption isotherms, the Langmuir and Freundlich models were used to fit the experimental sorption data.

Langmuir model is based on monolayer sorption and can be described by the following equation[37,38]:

$$C_e/q_e = 1/q_{\max}b + (1/q_{\max})C_e.$$

It assumes that the uptake of metal ions occur on a homogeneous surface by monolayer sorption without interaction between adsorbed ions. This means that there are uniform energies of adsorption on the surface. The Langmuir constant q_{\max} , obtained by plotting C_e/q_e against C_e is used to compare the performance of adsorbents. For a good adsorbent, a high q_{\max} is desirable. The q_{\max} for the pinecone is 25.86 mg/g. Thus, the pinecone is a good adsorbent. Similar results were obtained for the adsorption of Cd(II) ions using low cost adsorbents [11,12]. Adsorption coefficient, b (L/mg) relates to the apparent energy of adsorption. The lower the value of b , the more favourable the adsorption will be. The b and R_L values (as shown in Table 1) of Cd(II) show that the adsorption is favourable.

The Freundlich model is based on multilayer sorption and is given by the following equation[39,40]:

$$\log q_e = \log K_f + 1/n \log C_e,$$

Where q_e is the equilibrium sorption (mg/g) amount of Cd(II) adsorbed on Canola biomass, C_e is the equilibrium concentration of the adsorbate in aqueous solution (mg/L), K_f is a constant determined by plotting C_e/q_e versus C_e . K_f and $1/n$ are constants related to the sorption of adsorbent and intensity of the sorption respectively. Freundlich isotherm is used to estimate the adsorption intensity of the adsorbent towards the adsorbate by assuming that the adsorption occurs on a heterogeneous surface by multilayer sorption and that the amount of adsorbate adsorbed increases infinitely with increasing concentration. According to Balarak, n values between 1 and 10 represent favourable adsorption[19]. From the study, the n value of Cd(II) on Canola biomass suggests that the adsorption is favourable at studied conditions.

The experimental sorption data was more suited to the Freundlich isotherm with R^2 value of 0.943. This shows that the Freundlich model was able to adequately describe the relationship between C_e and q_e for the Cd(II). The calculated isotherm constants and correlation coefficients of Langmuir and Freundlich models are listed in the Table 1 below.

Error Functions

The usual way to validate the isotherms is to consider the goodness-of-fit using the linear regression coefficients, R^2 . However, using only the linear regression method may not be appropriate for comparing the goodness of fit of different isotherms. This is because an occurrence of the inherent bias resulting from linearization may affect the deduction. Therefore, in this study in addition to the linear regression analysis, the experimental data were tested

with two non-linear error functions: the sum-of-square error (SSE) and Chi square (χ^2) to determine the best fitting isotherm. The error functions are given[41,42]:

$$SSE = \frac{\sqrt{\sum(q_{exp} - q_{cal})^2}}{n}$$

$$\chi^2 = \frac{\sum(q_{exp} - q_{cal})^2}{q_{exp}}$$

The higher the value of R^2 and lower the values of error functions, the better is the goodness of-fit and therefore the applicability of the isotherm model. The values of these error functions obtained are given in Table 1. From the R^2 values and the results of the error analysis, Langmuir isotherm gave the best description of the Canola biomass/Cd(II) adsorption system, as it presented the highest linear regression value (0.998), and the lowest values for the other two error functions (Table 1).

Table 1: Results of isotherm parameters for the adsorption of Cd(II) onto Canola

Models	parameters		Model	parameters	
Langmuir	q_m	25.86	Freundlich	K_F	0.278
	K_L	0.724		n	3.842
	R^2	0.998		R^2	0.959
	χ^2	3.41		χ^2	14.28
	SSE	6.17		SSE	18.44

Adsorption Kinetics: In order to study the adsorption of CD(II) onto Canola biomass and to interpret the results, experimental data obtained were fitted to different kinetic models such as the pseudo-first-order and pseudo-second order.

The rate constant of adsorption is determined from pseudo first-order equation given by Lagergren, which is expressed as[43,44]

$$\text{Log}(q_e - q_t) = \text{log } q_e - \frac{k_1 t}{2.3}$$

where q_e and q_t are the amounts of the Cd(II) adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant adsorption (min^{-1}). Values of k_1 and q_e calculated from slope and the intercept of the plot of $\text{log}(q_e - q_t)$ versus t at different concentrations are given in Table 3. The results show that the values of R^2 were low and the experimental q_e values do not agree well with the calculated values (q_e , cal). This shows that the adsorption of the CD(II) onto Canola biomass does not follow first-order kinetics.

The pseudo second-order equation based on equilibrium adsorption can be expressed as[45,46];

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

where, k_2 (g/mg·min) is the adsorption rate constant of pseudo second-order adsorption rate. The value of q_e and k_2 can be obtained from the slope and intercept of the plot of t/q_t versus t respectively. The results show for all different initial concentrations of CD(II) studied with very high values of R^2 (Table 2) in addition to the good agreement between experimental and calculated values of q_e . Therefore, it can be said that the pseudo second-order kinetic model provided a good correlation for the adsorption of CD(II) onto Canola biomass in contrast to the pseudo first-order model.

Table 2: The adsorption kinetic model constants for the removal CD(II) onto Canola biomass

C ₀ (mg/L)	Pseudo second-order model					Pseudo first-order model			
	q _{e exp}	k ₂	R ²	q _{e cal}	SSE	K ₁	R ²	q _{e cal}	SSE
10	3.24	0.097	0.996	3.46	1.254	0.259	0.924	2.482	11.25
25	7.44	0.073	0.997	7.23	0.105	0.364	0.946	5.712	9.844
50	13.36	0.046	0.999	12.98	1.879	0.543	0.898	9.844	14.35
100	25.16	0.024	0.997	25.86	2.417	0.872	0.913	18.96	17.72

CONCLUSION

The present study investigated the adsorption of CD(II) from aqueous solution using Canola biomass in a batch system. Adsorption of CD(II) by Canola biomass is affected by operational parameters such as contact time, initial CD(II) concentration, adsorbent dosage and adsorbent particles. The equilibrium contact time was obtained as 75 min indicating that the adsorption process was a fast kinetic process. Kinetic and isotherm studies indicate that the adsorption of CD(II) was best described by the pseudo-second order kinetic equation and Langmuir isotherm equations respectively. This study has demonstrated that the low cost Canola biomass can be widely used for removal of CD(II) from aqueous solution.

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