

Adsorption of Pb(II) and Cd(II) metal ions from aqueous solutions by mustard husk

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Abstract

The adsorption of Pb(II) and Cd(II) metal ions on mustard husk has been found to be concentration, pH, contact time, adsorbent dose and temperature dependent. The adsorption parameters were determined using Langmuir and Freundlich isotherm models. The adsorption isotherm studies clearly indicated that the adsorptive behavior of Pb(II) and Cd(II) metal ions on mustard husk satisfies not only the Langmuir assumptions but also the Freundlich assumptions, i.e. multilayer formation on the surface of the adsorbent with an exponential distribution of site energy. Ion exchange and surface complexation are the major adsorption mechanisms involved.

The applicability of Lagergren kinetic model has also been investigated. Thermodynamic constant (k_{ad}), free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated for predicting the nature of adsorption. The results indicate the potential application of this method for effluent treatment in industries and also provide strong evidence to support the adsorption mechanism proposed.

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Keywords: Mustard husk; Metals ions; Adsorption; Wastewater; Isotherms; Kinetics

1. Introduction

The release of heavy metals into our environment is still large. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have toxic or other wise harmful effects on many forms of life. The numerous metals which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), zinc (Zn), manganese (Mn) and nickel (Ni), etc.

Considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials such as waste wool, nut wastes, tree barks, modified cotton and sawdust [1–5]. Many agricultural by products such as bark and sawdust are low cost (or of no economic value) materials. Activated carbon produced from almond shell [6], sawdust based GAC [7], tree bark treated with formaldehyde

and sulphuric acid [8], bone char, tea leaves, wood charcoal [9], coconut shell carbon [10], sulphurized activated carbon [11], ozonized activated carbon [12], chemically treated GAC [13] rice hulls and rice bran, pine bark, treated sawdust and agricultural waste [14,15] have been used with and without treatment for the removal of heavy metals.

Mustard husk from agriculture is often considered as waste material and widely available. Some preliminary investigations on the removal of heavy metal ions with sawdust have been reported [16], the present study undertakes the adsorption capacity of mustard husk for the removal of heavy metals from aqueous system.

2. Materials and methods

2.1. Experimental procedure

The mustard husk used in the present work obtained from nearby villages (Badh-Dhamasya) of Jaipur district, Rajasthan, India. In each experimental initial concentration of metal ions of 1.0, 2.0, 3.0, 4.0 and 5.0 mg/L were used. The untreated mustard husk was used as an adsorbent in the bench scale studies. Typi-

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cally, 0.6–1.2 g mustard husk was added in separate flasks each, containing 100 mL of the test solution of metal ions. The mixture of the test solution and mustard husk was stirred in a shaker at 120 rpm continuously for several hours. The contents were centrifuged and filtered through Whatman filter paper No. 41. The unabsorbed metal ions in the filtrate were estimated by atomic absorption spectrophotometer (AAS) using flame method.

The pH of the suspension in one set of experiment was adjusted with NaOH and HNO₃. The adsorption experiments were carried out at room temperature. The effect of pH, effect of initial concentration, contact time. The consumption of mustard husk, kinetics, temperature and isotherms were observed.

2.2. Instrumentation

GBC 932 AA atomic adsorption spectrometer (AAS) operating with an air acetylene flame was used to analyze the concentration of heavy metals. The minimum detection limit was equal to or less than EPA requirement. Standard solutions with concentrations of heavy metal ions in the linear range of the instrument were used to construct each calibration curve. During analysis of the samples for metal concentration, those samples in which the concentration of heavy metals was observed to be beyond the linear range of the references were diluted to appropriate concentrations. All measurements were repeated three times and those results in which the standard deviations were found greater than 0.1 mg/L were not accepted.

The pH measurements were performed is a controlled pH analyzer (LABINDIA). The pH meter was standardized using buffer solutions of pH values: 4, 7, and 9.

Micromeritics ASAP 2010 surface area analyzer and a mechanical shaker of WIDSONS SCIENTIFIC make was used for all the adsorption experiments for agitating the sample for a desired contact time.

2.3. Chemicals

Analytical grade reagents were used for heavy metal solution; ACS reagent grade concentrated nitric acid, NaOH and pH buffer solutions (E. Merck) were used to adjusted pH values of samples. In all experimental work, distilled demineralised water was used.

2.4. Adsorbate solution

Synthetic stock solution of heavy metals was prepared by dissolving required quantity of Analar grade salts in the distilled demineralised water. The salts used are cadmium chloride, lead nitrate for Cd(II), and Pb(II), respectively, for the preparation of stock solution. The stock solution was further diluted with distilled demineralised water to desired concentration for obtaining the test solutions.

2.5. Adsorbent

Mustard husk was collected during the harvest season from the villages (Badh-Dhamasya) of Jaipur district, Rajasthan, India and was used without any pre-treatment. It was properly char-

Table 1
Characteristics of the mustard husk

Parameters	Value
pH	8–8.5
Conductivity ($\mu\text{S cm}^{-1}$)	125
Salinity	0.0
Odour	None
Color	Light-yellowish
Bulk density (g/mL)	0.05
Moisture (%)	11
BET surface area (m^2/g)	0.27
Langmuir surface area (m^2/g)	0.32
Carboxylic functional group (mequiv./g CA)	Present
Lactic acid functional group (mequiv./g CA)	Present
Phenolic functional group (mequiv./g CA)	Present
Lignin	Present
Cellulose	Present
Sulphur	Present

acterized for a few parameters before conducting experiments (shown in Table 1).

3. Results and discussion

3.1. Effect of initial concentration of heavy metal

The effect of initial concentration on the percentage removal of Pb(II) and Cd(II) by mustard husk is shown in Fig. 1. It is apparent from the figure the percentage removal decreases with the increase in the Pb(II) and Cd(II) concentration. For Pb(II) and Cd(II) at same adsorbent dose and contact time, a slight drop in percentage removal at higher was observed concentration. At low concentrations, sufficient adsorption sites are available for adsorption of the Pb(II) and Cd(II) metal ions. Therefore, the fractional adsorption was observed to be independent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence the percentage removal of Pb(II) and Cd(II) depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration. The difference in percentage removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent.

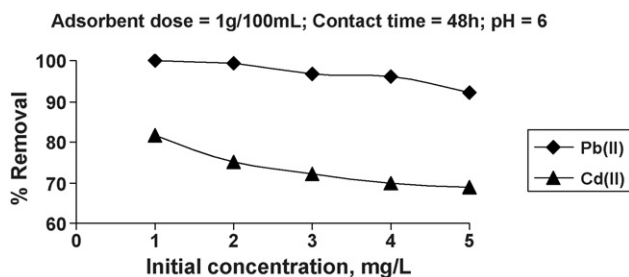


Fig. 1. Effect of initial concentration vs. percentage removal Pb(II) and Cd(II) by mustard husk.

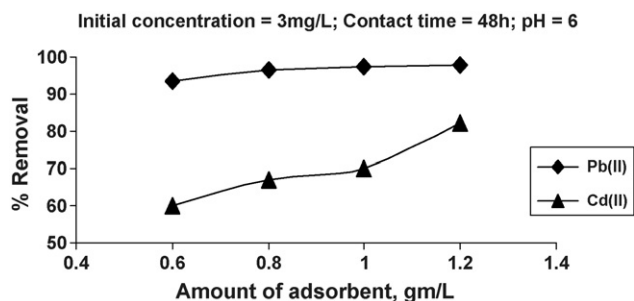


Fig. 2. Effect of adsorbent dose on percentage removal Pb(II) and Cd(II) for mustard husk.

3.2. Effect of adsorbent dose

The results for adsorptive removal of Pb(II) and Cd(II) with respect to adsorbent dose are shown in Fig. 2 over the range 6–12 g/L, at pH 6. It was observed that there was a slight increase in percentage removal of Pb(II) and Cd(II) ions with adsorbent dose due to the greater availability of the exchangeable sites or surface area. Moreover the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions.

3.3. Effect of contact time

Fig. 3 shows the effect of contact time on the percentage removal of Pb(II) and Cd(II) using 10 g/L of mustard husk at pH 6, for the initial concentration of 3 mg/L of each metal ions. The percentage removal of Pb(II) and Cd(II) increases with increase of contact time till equilibrium is attained.

It is observed that in case of Cd(II) ions there is a sharp increase in percentage removal with increasing contact time reaching nearly 99% removal at 72 h, on other hand percentage removal of Pb(II) increases gradually with contact time, reaching nearly 100% removal at 72 h.

3.4. Effect of pH

pH is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. Fig. 4 shows the effect of pH on Pb(II) and Cd(II) removal efficiencies of mustard husk. These studies were conducted at a constant initial metal ion concentration of 3 mg/L, adsorbent

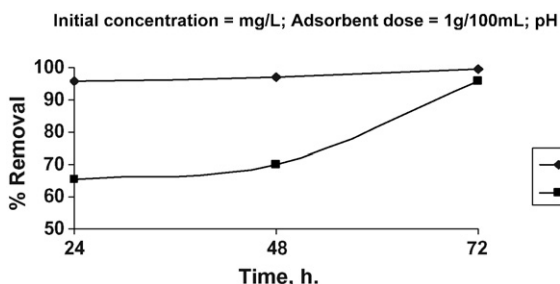


Fig. 3. Effect of contact time on percentage removal of Pb(II) and Cd(II) for mustard husk.

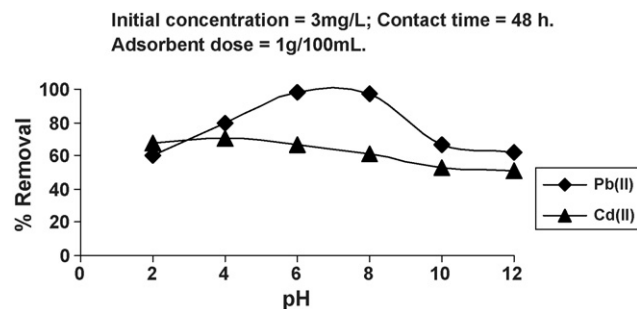
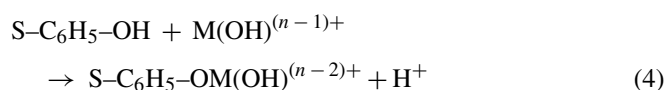
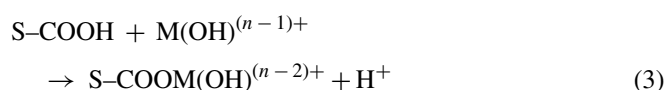
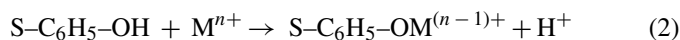


Fig. 4. Effect of pH on percentage removal Pb(II) and Cd(II) for mustard husk.

dose 10 g/L solution and agitation period of 48 h for both metal ions under varying pH on mustard husk.

The percentage adsorption increases with pH 4 to attain a maximum at pH 6 and thereafter it decreases with further increase in pH. The maximum removal of Pb(II) at pH 6 as found to be nearly 97%, whereas, for Cd(II) 70% removal at pH 4 was observed.

The effect of pH can be explained in term of pH_{zpc} (zero point of charge) of mustard husk is at 6.0 and below this pH, the surface charge of the adsorbate is positive. On the other hand, at pH less than pH_{zpc} , the predominant metal species $[M^{n+}$ and $M(OH)^{(n-1)+}]$ are positively charged; therefore uptake of metals in the pH range of 2–6 is a $H^+ - M^{n+}$ exchange process [17]. The possible sites on mustard husk for specific adsorption includes H^+ ions in $-C_6H_5-OH$ and $-COOH$ functional groups in which H^+ ions can be exchanged for cations in solution.



where S denotes the surface,

However, the sites responsible for the adsorption process are not exclusively due to the $COOH$ and $-C_6H_5-OH$ groups. Other sites on the mustard husk can also contribute to the adsorption process. In acidic medium the electrometric effect of the amide group in mustard husk leads to surface protonation and possesses not positive charge on the surface. These H^+ ions from the surface are also exchange with positively charged sorbate species with subsequent coordination of a metal ion.

An increase in pH above pH_{zpc} shows a slight in adsorption in which the surface of the adsorbent is negatively charged and the sorbate species are still positively charged. As the adsorbent surface is negatively charged as well, the increasing electrostatic attraction between positive sorbate species and adsorbent particles would lead to increase adsorption of metal ions. This is in accordance with the earlier observations. Decrease in removal of metal ions at lower pH is apparently due to the higher

concentration of H^+ ions present in the reaction mixture, which compete with the M^{2+} ions for the adsorption sites of mustard husk. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes [18–24].

The increase in metal removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal cations for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and the metal ions. Decrease in adsorption at higher pH (above pH 6) is due to the formation of soluble hydroxyl complexes [12]. The difference in adsorption behavior of different heavy metal ions may be because of difference in their ion exchange capacity on the surface depending on their charge density, extent of hydrolysis and solubility of hydrolyzed metal ions in solution under present experimental condition.

3.5. Effect of temperature

Fig. 5 shows the experimental results obtained from a series of contact time studies for metal ions adsorption with an initial metal ions concentration of 3 mg/L in which temperature was varied from 20 to 60 °C. The adsorption of metal ions has been found to increase with an increase in temperature from 20 to 60 °C. The increase in adsorption capacity of mustard husk with temperature indicates an endothermic process. The increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. At higher temperatures the possibility of diffusion of solute within the pores of the adsorbent may not be ruled out as reported by earlier workers for the adsorption of cations on GAC. Since diffusion is an endothermic process greater adsorption will be observed at higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperatures. The above results were further substantiated by the various thermodynamic parameters evaluated of adsorption.

The thermodynamic parameters such as free energy change (ΔG), enthalpy changes (ΔH), and entropy change (ΔS) were determined using the following equations and presented in Table 2:

$$K_c = \frac{C_{Ac}}{C_e} \quad (5)$$

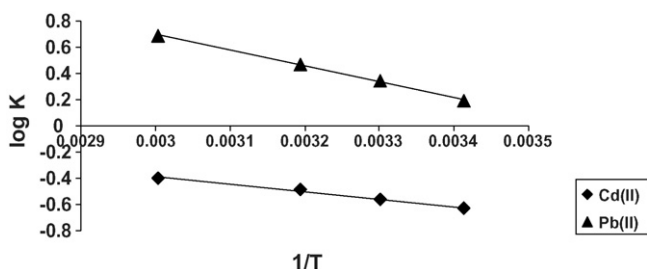


Fig. 5. Plot of $\log_{10} K$ vs. $1/T$ for Pb(II) and Cd(II) by mustard husk.

Table 2

Equilibrium constants and thermodynamic parameters for the adsorption of Pb(II) and Cd(II) metal ions on mustard husk

Metal ions	Temperature (°C)	K_e	ΔG (kJ/mol)	ΔS (kJ/mol K)	ΔH (kJ/mol)
Pb(II)	20	1.56	-1.11	0.09	26.01
	30	2.21	-1.99	0.09	
	40	2.9	-2.77	0.091	
	60	4.9	-4.40	0.091	
Cd(II)	20	0.971	0.0706	0.0252	7.4612
	30	1.053	-0.1321	0.0250	
	40	1.15	-0.3637	0.025	
	60	1.4	-0.931	0.0252	

Amount of adsorbent = 1 g/100 mL; contact time = 24 h; initial concentration = 3 mg/L.

where K_c is the equilibrium constant, C_{Ac} and C_e are the equilibrium concentration (mg/L) of the metal ion on adsorbent and in the solution, respectively. The free energy change (ΔG) was calculated from the relation:

$$\Delta G = -RT \ln K_c \quad (6)$$

where T is the temperature in kelvin (273 K) and R is the gas constant (8.314×10^{-3} kJ/mol K). Enthalpy change (ΔH) was calculated from the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (8)$$

ΔH and ΔS were obtained from the slope and intercept of Vant Hoff plots of $\log K_c$ versus $1/T$ (Fig. 5). Positive values of ΔH thermodynamically substantiate the assumption that the adsorption of metal ions on the mustard husk is endothermic. The negative values of ΔG indicate feasibility and spontaneous nature of adsorption of metal ions on the adsorbent. ΔS is estimated to be very small in the experimental conditions. Therefore, the entropic change occurring from adsorption is thought to be negligible.

3.6. Adsorption kinetics

Kinetics is another important aspect in any evaluation of sorption as a unit operation. The kinetic constants of metal adsorption, which could be used to optimize the residence

$$\log_{10}(q_e - q) = \log_{10}q_e - \frac{K_{ad}t}{2.303} \quad (9)$$

time of an industrial wastewater mustard husk, were computed using the above experimental data. The adsorption kinetics of heavy metal ion adsorption on mustard husk follows first order rate expression given by Lagergren [24].

$$Q_e = (C_0 - C_e) \frac{V}{M} \quad (10)$$

where K_{ad} (1/h) is the rate constant of adsorbent, q and q_e are the amount of heavy metal ions adsorbed (mg/L) at time t (h) and equilibrium time. Linear plots of $\log_{10}(q_e - q)$ versus t (Fig. 6)

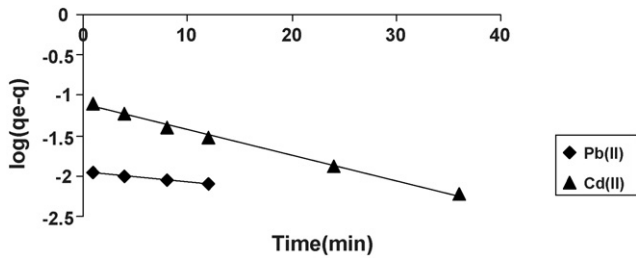


Fig. 6. Plot for Lagergren rate constant of Pb(II) and Cd(II) by mustard.

show the applicability of above equation for mustard husk. The K_{ad} values at metal ion concentrations were calculated from the slope of linear plots and presented in Table 3. The K_{ad} values were comparable with recently reported values for Pb(II) and Cd(II) metal ions removal by mustard husk.

The initial adsorption kinetic coefficients γ (1/mg h) were also computed as per [25] and are presented in Table 3

$$\gamma = \left(\frac{dc}{dt} \right)_t \frac{V}{mC_0} \quad (11)$$

where t is the time (h), C the metal ion concentration at time (t), V the solution volume (L), m the mustard husk weight (mg), and C_0 is the initial concentration (mg/L).

3.7. Adsorption isotherms

The adsorption studies were conducted at fixed initial concentration of Pb(II) and Cd(II) by varying adsorbent dosage. The equilibrium data obtained were analyzed in the light of Langmuir and Freundlich isotherms.

The Freundlich equation is given by [26]:

$$\frac{x}{m} = KC_e^{1/n} \quad (12)$$

Taking the logarithmic form of the equation:

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \quad (13)$$

Langmuir equation is given by [27]:

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \quad (14)$$

or,

$$\frac{x}{m} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{a} \quad (15)$$

Table 3
Kinetics constants for pb(II) and Cd(II) metal ions adsorption

Metal ions	Adsorption rate constant, K_{ad} ($\times 10^{-2}$ 1/h)	Initial adsorption coefficient, γ (1/mg min)
Pb(II)	2.85	7.192
Cd(II)	7.30	7.196

Amount of adsorbent = 1 g/100 mL; temperature = 30 °C; initial concentration of metal ions = 3 mg/L.

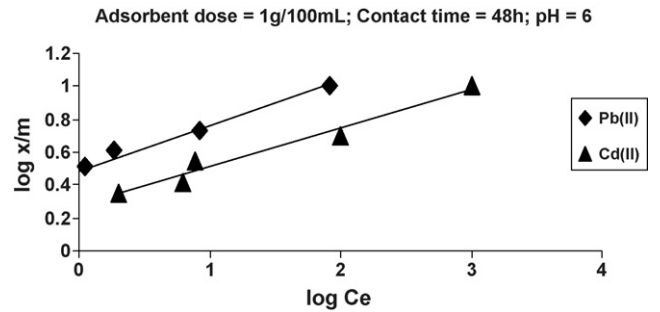


Fig. 7. Freundlich adsorption isotherm of Pb(II) and Cd(II) by mustard.

Table 4
Values of Langmuir and Freundlich isotherm constants for adsorption of Pb(II) and Cd(II) metal ions

Metal ions	a (mg/g)	b (l/mg)	R^2	R_L
Langmuir constants				
Pb(II)	30.48	0.52	0.9977	0.38
Cd(II)	42.85	0.28	0.9955	0.26
Metal ions	K_e	n	R^2	
Freundlich constants				
Pb(II)	1.41	2.87	0.9905	
Cd(II)	1.62	2.63	0.9927	

Amount of adsorbent = 1 g/100 mL; contact time = 48 h.

where x/m is the amount of Pb(II) and Cd(II) metal ions adsorbed per unit mass of adsorbent in mg/g, C_e the equilibrium concentration of heavy metal ions in mg/L, K_e and n the Freundlich constants, a a Langmuir constant which is a measure of adsorption capacity expressed in mg/g, and b is also Langmuir constant which is a measure of energy of adsorption expressed in l/mg. The parameters a and b have been calculated from the slope and the intercept of the plots.

Fig. 7 gives the Freundlich adsorption isotherm plot of $\log x/m$ versus $\log C_e$. The values of K_e and $1/n$ obtained from intercept and slope of the plot are given in Table 4.

The Langmuir adsorption isotherm plot for m/x versus $1/C_e$ is shown in Fig. 8 and the plots show two distinct regions, one for low $1/C_e$ values up to about 25 l/mg and another for

$$R_L = \frac{1}{1 + bC_i} \quad (16)$$

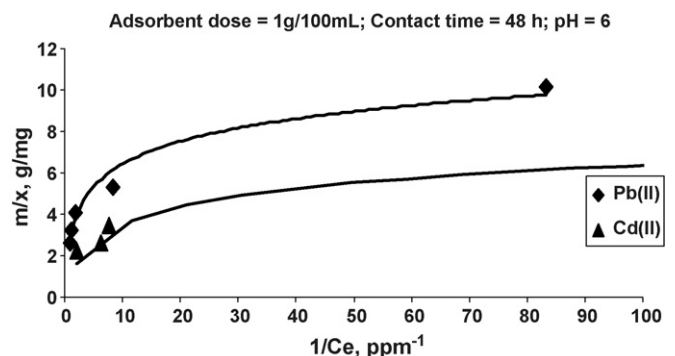


Fig. 8. Langmuir adsorption isotherms of Pb(II) and Cd(II) by mustard husk.

higher $1/C_e$ values. The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant R_L , which is defined as, where C_i is the initial concentration of heavy metal ions (mg/L) and b is Langmuir constant which indicates the nature of adsorption. The separation factor R_L indicates the isotherm shape and whether the adsorption is favorable or not, as per the criteria given below.

R_L values	Adsorption
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of Langmuir constants ' a ', ' b ' and R_L are presented in Table 4. Since R_L values lie between 0 and 1 for all three adsorbents studied, it is seen that the adsorption of Pb(II) and Cd(II) metal ions is favorable [28].

Adsorption capacity as indicated by value of ' a ' is seen to be maximum for mustard husk i.e. Cd(II) (42.85 mg/g), and Pb(II) (30.48 mg/g) with a much lower capacities. The energies of adsorption, as indicated by ' b ' are seen to be highest for Pb(II) (0.521/mg), and Cd(II) (0.281/mg) in that order. The values of n lie between 1 and 10 indicating favorable adsorption [24]. K_c seen to be Cd(II) > Pb(II). This gives a similar inference as that obtained from Langmuir isotherms.

On the basis of regression analysis of the experimental data on the adsorptive behavior of metal ions on mustard husk, it may be inferred that the adsorption behavior of metal ions on mustard husk is in good agreement with Langmuir model. These can be attributed to three main causes: (i) the formation of monolayer coverage on the surface of mustard husk with minimal interaction among molecules of substrate, (ii) immobile and localized adsorption, and (iii) all sites having equal adsorption energies. The shapes of isotherms suggest that there are high-energy adsorption sites to favor strong adsorption at low equilibrium concentrations for the mustard husk [20–24].

Various mechanisms and steps in adsorption phenomena can control the kinetics for major rate limiting steps are generally cited (1) mass transfer of solute from solution to the boundary film; (2) mass transfer of metal ions from boundary film to surface; (3) sorption of ions onto sites; and (4) internal diffusion of solute. The third step is assumed to be very rapid and non-limiting in this kinetic analysis. Sorption is a rapid phenomenon. The first and second steps are internal mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. The fourth one is an intra particle diffusion resistance step [29,30].

4. Conclusions

The following conclusions can be drawn based on investigation of heavy metal ions removal by mustard husk adsorption.

(a) Mustard husk appears to be a promising adsorbent for removal of Pb(II) and Cd(II) metal ions from wastewa-

ter. At these adsorption levels, a process using mustard husk for the removal and recovery of a heavy metal is potentially more economical than current process technology.

- (b) Adsorption of Pb(II) and Cd(II) metal ions is dependent on its initial concentrations, the amount of mustard husk, contact time and pH of metal solution. Maximum removal of metal ions on mustard husk is at pH 6 (Pb) and 4 (Cd). Since different metals have different properties with regard to acidity of the solution, optimized pH for different metals removal may be very different. A further study on some other metals will be needed.
- (c) Isothermal data of metal ion sorption on mustard husk can be modeled by both Freundlich and Langmuir isotherms. The capacity of mustard husk for adsorption of certain metals can be calculated by using these models. The adsorption capacity of mustard husk for Cd(II) 42.85 mg/g and Pb(II) 30.48 mg/g.

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