Removal of cadmium from wastewater using agricultural waste 'rice polish'

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Abstract

A novel biosorbent rice polish has been successfully utilized for the removal of cadmium(II) from wastewater. The maximum removal of cadmium(II) was found to be 9.72 mg g^{-1} at pH 8.6, initial Cd(II) concentration of 125 mg l^{-1} and temperature of 20 °C. The effect of different parameters such as contact time, adsorbate concentration, pH of the medium and temperature were investigated. Dynamics of the sorption process were studied and the values of rate constant of adsorption, rate constant of intraparticle diffusion and mass transfer coefficient were calculated. Different thermodynamic parameters, viz., changes in standard free energy, enthalpy and entropy have also been evaluated and it has been found that the reaction was spontaneous and exothermic in nature. The applicability of Langmuir isotherm showed monolayer coverage of the adsorbate on the surface of adsorbents. A generalised empirical model was proposed for the kinetics at different initial concentrations. The data were subjected to multiple regression analysis and a model was developed to predict the removal of Cd(II) from wastewater.
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1. Introduction

Minimizing water pollution by toxic heavy metals resulting from human technological activities is challenging. Biosorption can be part of the solution. Biosorption of heavy metals by bacterial fungal or algal biomass (live or dead cells) and agricultural waste biomass [1–10] has been recognized as a potential alternative to existing technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for removal of heavy metals from industrial wastewater because these processes have technical and/or economical constraints.

The literature reveals two distinct approaches to the use of living organisms and the use of a non-viable biomass [11–13]. There are significant practical limitations to the method, which employ living systems. Perhaps the most significant limitation is that microbial growth is inhibited when the concentrations of metal ions are too high or when significant amount of metal ions are adsorbed by microorganisms [11]. Dead cells or agricultural wastes accumulate heavy metal ions to the same or to a greater extent than living cells [11–13]. The reason for this is that the changes, which occur in the cell structure after the cells are dry-killed, affect adsorption in a positive manner [14]. For metal removal applications, the use of dead biomass or agricultural waste may be preferable as large quantities are readily and cheaply available as a byproduct of various industries [15]. Therefore we have chosen rice polish (rice bran) for the removal of Cd(II) from wastewater; because rice bran is cheap, easily available and mostly biodegradable.

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2. Materials and methods

2.1. Physico-chemical analysis of the adsorbent

Rice polish is a byproduct of a rice milling plant. Rice polish is biodegradable. Our sample were collected from M/s Manoj Industries (rice mill), Chunar, Mirzapur (UP), and was used in experiments with double washing with double distilled water to remove soluble lighter materials and drying at 60 °C in an oven and crushing and sieving to <178 μm.

Various physical properties of rice polish are given in Table 1. Chemical analysis of the rice polish showed the presence of various oxides of Ca, Si, Mn, Mg, and Fe, etc. X-ray diffraction and IR studies showed that major constituents of rice polish were carbon while quartz, carbon hexagonal, Fe–O, Mg–O, Mn–O, Ca–O, Si–C, $CaSiO_3$, Ca_2SiO_4 and Ca–P have been found to be 18.44%.

2.2. Experimental procedure

In the present investigation, the batch mode of operation was selected in order to measure the progress of adsorption. The same was carried out by shaking 1.0 g of desired grade of adsorbent (rice polish) with 50 ml aqueous solution of adsorbate (cadmium chloride) of different concentrations (100, 125 and 150 mg l^{-1}) at different temperatures (20, 30 and 40 °C) and different pH (4.0, 6.4, 7.0, 8.6 and 10.0) in different glass bottles in a shaking thermostat at a constant speed of 125 rpm. The pH of the adsorbate solution was adjusted by adding HCl or NaOH. The progress of adsorption was noted at different time intervals till the attainment of saturation. At the completion of predetermined time intervals, the adsorbate and adsorbent were separated by high speed centrifugation at 15,000 rpm and the supernatant liquid was analysed by the Orion Ion Selective Titrator plus System, model no. 960, made by Thermo Orion (USA) to determine the residual concentration of cadmium ion.

Blank samples were run under similar conditions of concentration, pH and temperature but without the adsorbent in all cases to correct for any adsorption on the internal surface of the bottles.

Table 1
Physical and chemical properties of biosorbent rice polish

Surface area (m^2 g^{-1})	452.00
Bulk density (g cm^{-3})	0.30
Particle size (μm)	<178
Average particle diameter (cm)	2.24×10^{-2}
Porosity	0.39
Proximate analysis	
Moisture (%)	8.30
Volatile matter (%)	43.12
Fixed carbon (%)	30.14
Ash (oxides of Ca, Mn, Si, Fe, Mg, etc.) (%)	18.44

3. Results and discussion

3.1. Effect of contact time and concentration

A series of experiments were performed at different initial adsorbate concentrations, viz., 100, 125 and 150 mg l^{-1} and time interval and at a temperature of 30 °C and pH 8.6. The percentage removal of Cd(II) was found to be 96.95, 92.15 and 85.80, respectively. The results showed (Fig. 1) that the extent of adsorption increased rapidly in the initial stages but became slow in the later stages till the attainment of equilibrium and Fig. 1 also showed that the removal was highly dependent on the concentration of the adsorbate. The removal curves thus obtained are single smooth and continuous suggesting the formation of monolayer of adsorbate on the surface of the adsorbent [16,17]. Equilibrium time for the adsorption of Cd(II) on rice polish at various adsorbate concentrations was found to be 90 min, which showed that equilibrium time was independent of initial adsorbate concentration. The following correlation had been developed between percentage removal and initial adsorbate concentrations (C_0) to predict successfully the percentage removal of Cd(II) by rice polish at any initial concentrations.

Percentage removal of Cd(II) = $1.68 C_0^{0.032}$.

3.2. Adsorption dynamics

The rate constant for the adsorption (k_{ad}, min^{-1}) of cadmium ion was evaluated in the light of Lagergren rate equation [18]:

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303} t \qquad (1)$$

where q and q_e are the amounts of adsorbate (mg g^{-1}) at time t (min) and at equilibrium, respectively. The linear plots of $\log(q_e - q)$ versus t (Fig. 2) suggest the first order kinetics of the uptake of Cd(II). The values of k_{ad} at different temperatures were calculated from the slopes of these curves and are provided in Table 1.

The data was also tested for intraparticle diffusion using the following equation [19]:

$$q = k_{id} t^{1/2} \qquad (2)$$

where k_{id} is the rate constant for intraparticle diffusion. It is evident from Fig. 3 that the plot q versus $t^{1/2}$ was linear with in a certain extent but did not pass through the origin. It appeared that the pore diffusion was not the only rate controlling step [20,21] in the removal of Cd(II). The values of k_{id} at different temperatures have been calculated from the slopes of these graphs and are represented in Table 2, which is further supported by calculating the intraparticle diffusion co-efficient ($\bar{D}$) using the following equation [21]:
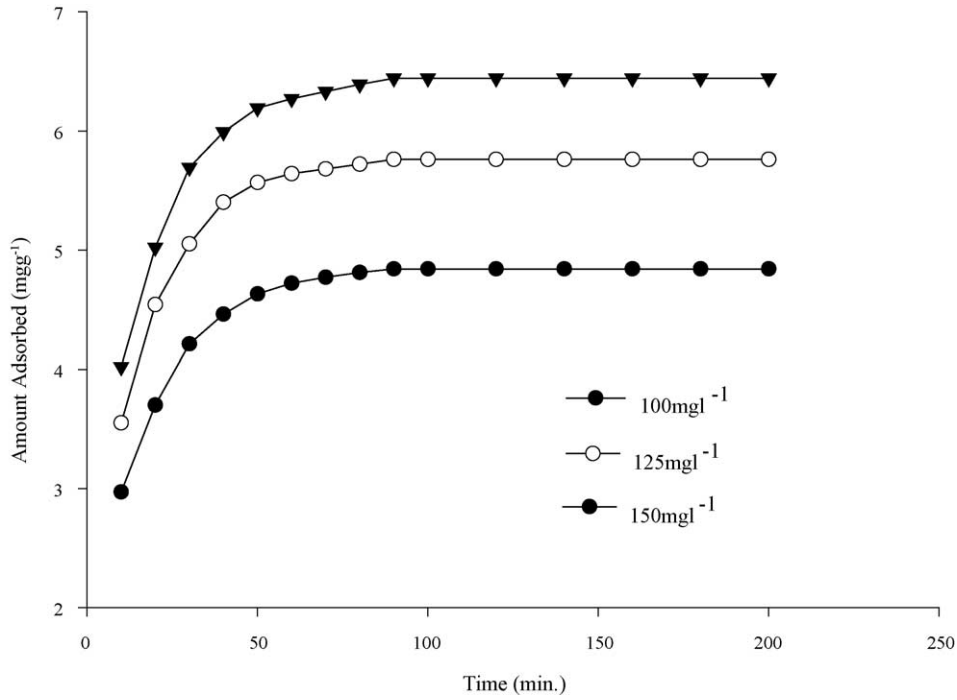
$$\bar{D} = \frac{0.03 r^2}{t_{1/2}} \qquad (3)$$

Fig. 1. Time variation plot for adsorption of Cd(II) on rice polish at initial concentration 100, 125 and 150 mg l^{-1}. Conditions: particle size, <178 μm; temperature, 30 °C; pH, 8.6; agitation rate, 125 rpm.
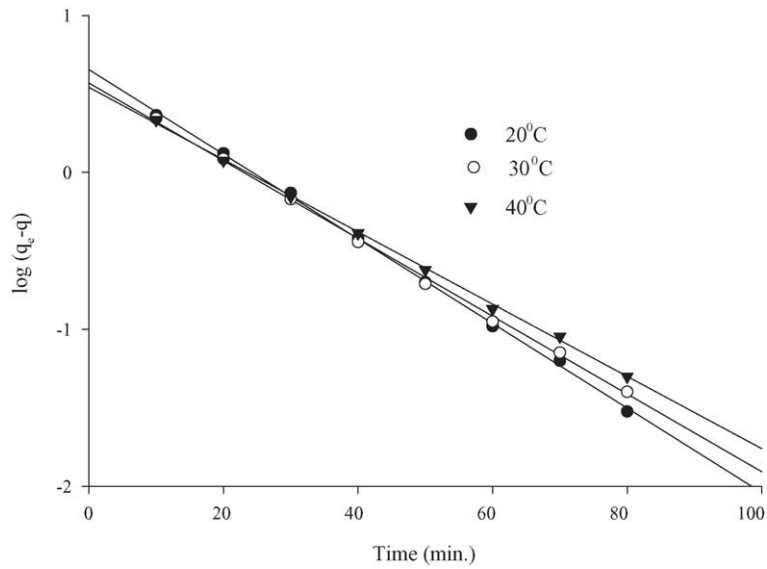

Fig. 2. Rate constant plot for adsorption of Cd(II) on rice polish at 20, 30 and 40 °C. Conditions: concentration, 125 mg l^{-1}; particle size, <178 μm; pH, 8.6; agitation rate, 125 rpm.

Table 2
Adsorption rate constants for Cd(II) at different temperatures

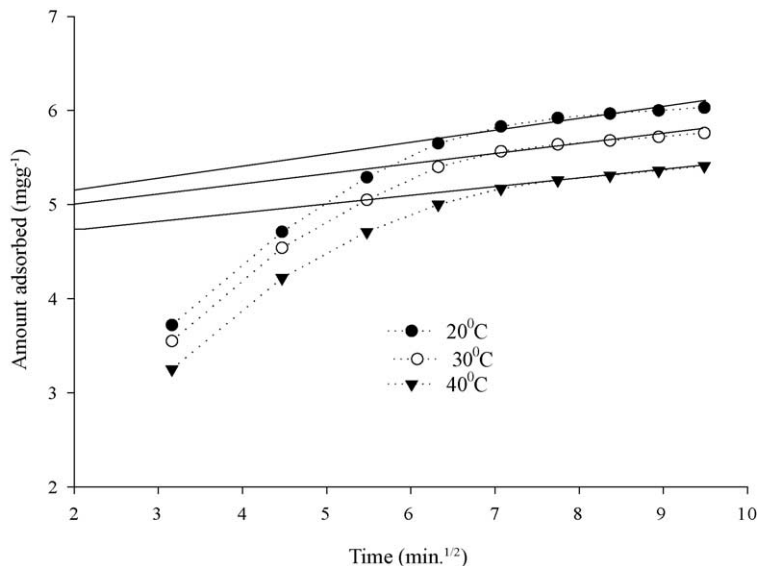| Temperature (°C)	k_{ad} (min^{-1})	k_{id} (mg g^{-1}, min$^{-1/2}$)	$\bar{D}$ (cm^2 s^{-1})	β_1 (cm s^{-1})
20	6.080×10^{-2}	1.192×10^{-2}	8.315×10^{-9}	6.892×10^{-5}
30	5.711×10^{-2}	1.201×10^{-2}	7.426×10^{-9}	6.479×10^{-5}
40	5.366×10^{-2}	8.364×10^{-3}	5.743×10^{-9}	5.925×10^{-5}

Fig. 3. Intraparticle diffusion plot for adsorption of Cd(II) on rice polish at 20, 30 and 40 °C. Conditions: concentration, 125 mg l^{-1}; particle size, <178 μm; pH, 8.6; agitation rate, 125 rpm.

where r (cm) is the average radius of the adsorbent particle and $t^{1/2}$ (min) the time for half of the adsorption. According to the Michelsen et al. [22] a $\bar{D}$ value of the order of 10^{-11} cm^2 s^{-1} is indicative of intraparticle diffusion as rate determining step. In this investigation, the values of $\bar{D}$ (Table 2) obtained was in order of 10^{-9} cm^2 s^{-1} which was more than two orders of magnitude higher, indicated that the intraparticle diffusion was not the only rate controlling step [22]. It was concluded that both boundary layer and intraparticle diffusion might be involved in this removal process.

3.3. Mass transfer analysis

The mass transfer analysis for the adsorption of cadmium(II) ion was determined at various temperatures (20, 30 and 40 °C) using the following equation [23]:

$$\ln \left(\frac{C_t}{C_0} - \frac{1}{1 + mK} \right)$$
$$= \ln \left(\frac{mK}{1 + mK} \right) - \left(\frac{1 + mK}{mK} \right) \beta_1 S_s t \qquad (4)$$

where C_0 is the initial adsorbate concentration, C_t the adsorbate concentration after time t, m the mass of the biosorbent per unit volume, K the constant obtained by multiplying Q^0 and b (Langmuir's constants), β_1 the mass transfer coefficient, and S_s the outer specific surface of the adsorbate per unit volume.

The values of β_1 (Table 2) at different temperatures (20, 30 and 40 °C) calculated from the slopes and the plots of $\ln(C_t/C_0 - 1/1 + mK)$ versus t (Fig. 4) suggest that the rate of mass transfer of Cd(II) on to rice polish was rapid enough

[24] to use this adsorbent for the treatment of wastewater rich in cadmium.

3.4. Effect of temperature

Experiments were also performed at different temperatures 20, 30 and 40 °C. The percentage of adsorption decreased from 97.20 to 86.35 with the rise in temperature from 20 to 40 °C at a concentration of 125 mg l^{-1} and a pH of 8.6 (Fig. 5). Equilibrium time for 20, 30 and 40 °C was found to be 90 min indicating thereby that the equilibrium time was independent of the temperature. The above results showed the exothermic nature of the adsorption [1,25]. The decrease in adsorption with the rise in temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phase [26].

The variation in the extent of adsorption with respect to temperature has also been explained on the basis of thermodynamic parameters, viz., changes in standard free energy (ΔG°) and enthalpy (ΔH°) and entropy (ΔS°). These were calculated by using the following equations [27]:

$$\text{(i)} \quad \Delta G^\circ = RT \ln K_c \qquad (5)$$

$$\text{(ii)} \quad \Delta H^\circ = R \left(\frac{T_1 T_2}{T_2 - T_1} \right) \ln \frac{K_{c_2}}{K_{c_1}} \qquad (6)$$

$$\text{(iii)} \quad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \qquad (7)$$

where R is the gas constant, T the temperature on the absolute scale and K_c, K_{c_1}, and K_{c_2} the equilibrium constants at temperature T, T_1 and T_2, respectively. The values of these parameters thus calculated are recorded in Table 3. It is
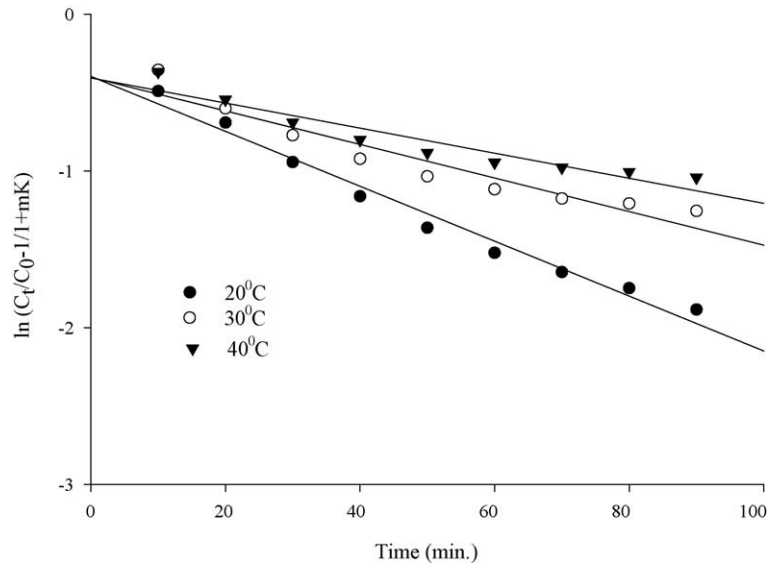
Fig. 4. Mass transfer plot for adsorption of Cd(II) on rice polish at 20, 30 and 40 °C. Conditions: concentration, 125 mg l^{-1}; particle size, <178 μm; pH, 8.6; agitation rate, 125 rpm.
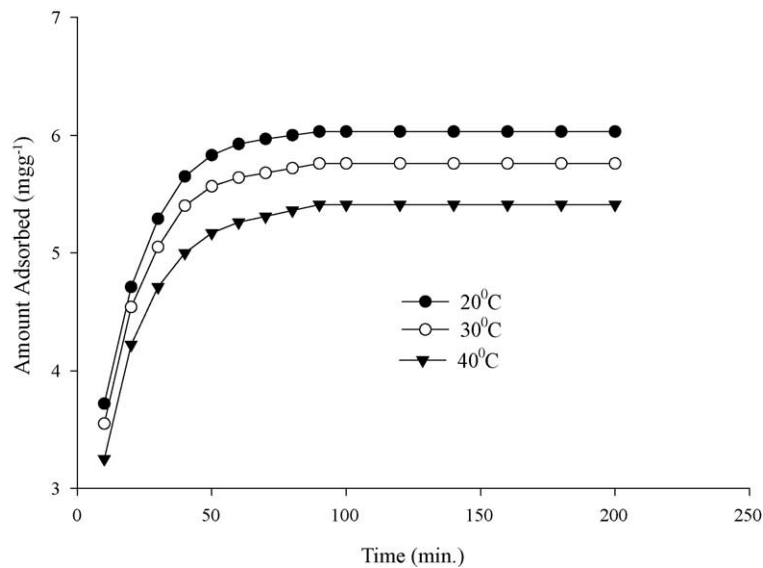

Fig. 5. Time variation plot for adsorption of Cd(II) on rice polish at 20, 30 and 40 °C. Conditions: concentration, 125 mg l^{-1}; particle size, <178 μm; pH, 8.6; agitation rate, 125 rpm.

obvious from this table that the negative and small values of free energy change (ΔG) is an indication of spontaneous nature of the adsorption process. The negative values of standard enthalpy change (ΔH°) for the intervals of temperatures showed the exothermic nature of the adsorption process and the negative values of ΔS° for the corresponding temperature intervals suggested the probability of favorable adsorption.

3.5. Adsorption isotherm

In the present investigation the data has been found to fit the Langmuir isotherm. The basic assumption of Langmuir adsorption isotherm is based on a monolayer coverage of the adsorbate on the surface of adsorbent. The saturated monolayer is represented by the following equation

Table 3
Thermodynamic parameters for adsorption of Cd(II) on rice polish at different temperatures

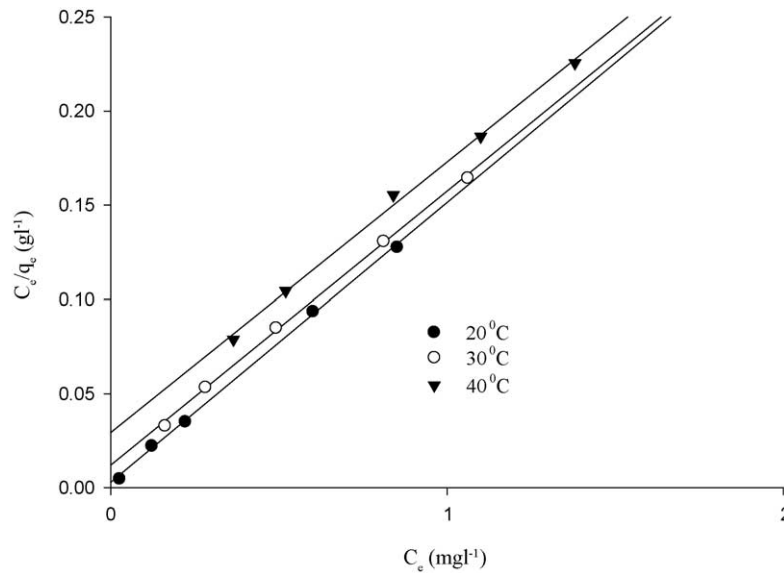| Temperature (°C)	$-\Delta G^{\circ}$ (kcal mol^{-1})	$-\Delta H^{\circ}$ (kcal mol^{-1})	$-\Delta S^{\circ}$ (cal mol^{-1} K^{-1})
20	2.048	18.589	56.454
30	1.484		
40	1.141	11.853	34.220

Fig. 6. Langmuir isotherm plot for adsorption of Cd(II) on rice polish at 20, 30 and 40 °C. Conditions: concentration—100, 110, 125, 140 and 150 mg l^{-1}; particle size—<178 μm; pH—8.6; agitation rate—125 rpm.

[28]:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad (8)$$

where C_e is the equilibrium concentration of the adsorbate, q_e the amount of the adsorbed adsorbate at equilibrium, Q^0 and b the Langmuir's constants related to the capacity and energy of the adsorption, respectively. The linearity of the plots C_e/q_e versus C_e (Fig. 6) suggested the applicability of Langmuir isotherm for the present system. Q^0 and b were determined from the slopes and intercepts of the respective plots and provided in Table 4. The values of Q^0 and b decreased with increase in temperature [1,25,29].

Heat of adsorption (ΔH) of the Cd(II) on rice polish was determined using the following equation [30]:

$$\ln b = \ln b' - \frac{\Delta H}{RT} \qquad (9)$$

where b (mg l^{-1}) is the Langmuir constant related to the energy of adsorption, b' the constant and R and T (K) the gas constant and temperature, respectively. A negative value (-7.075 kcal mol^{-1}) of ΔH confirmed the exothermic nature of the process.

The equilibrium parameter R_L which is defined as $R_L = 1/(1 + bC_i)$ in the range $0 < R_L < 1$ reflects the favorable adsorption process [30]. In the present investigation the equilibrium parameter is found to be in the range $0 < R_L < 1$ which

Table 4
Values of Langmuir constants and R_L for Cd(II)

Temperature (°C)	Q^0 (mg g^{-1})	b (l mg^{-1})	R_L
20	0.801	39.012	0.017
30	0.767	27.951	0.019
40	0.742	13.753	0.046

is shown in Table 4 indicating that the adsorption process was very favorable and the adsorbent exhibited a good potential [31].

3.6. Effect of pH

Experiments were performed at different pH (4.0, 6.4, 7.0, 8.6 and 10.0). The removal increased from 40.90 to 92.15% with an increase of pH from 4.0 to 8.6 and thereafter removal decreased from 92.15 to 19.75 with an increase of pH from 8.6 to 10.0, at temperature 30 °C and concentration 125 mg l^{-1}. The optimum pH for the removal of Cd(II) on rice polish was 8.6 (Fig. 7). It can be explained on the basis of the nature of sorbent used which contain several metal oxides. These oxides when mixed up with adsorbate solution undergo surface hydroxylations and form hydroxyl compounds on the surface which ultimately gives positively or negatively charged surface as a result of subsequent acid base dissociation [32]. Fig. 7 shows that the adsorption of cadmium was higher in alkaline pH. However, the removal was less in acidic range and reached a maximum around pH 8.6. In addition to this effect, the adsorbent surface is highly protonated in acidic medium, which is not favorable for cadmium uptake because in this medium, Cd^{++} is the dominant ion [24]. As a result the adsorption of cadmium is hindered due to electrical repulsion. As pH increases the degree of protonation of surface reduces gradually and approaches zero at pH 7.0 resulting in a gradual increase in the adsorption. Above pH 7.0 where Cd^{++} and CdOH$^+$ species are present in solution [24], the adsorbent surface starts acquiring a net negative charge making the situation electrostatically favorable for a higher uptake of cadmium. Above pH 8.6 removal of cadmium started to decrease due to soluble hydroxy complexes of cadmium hydroxides [33].
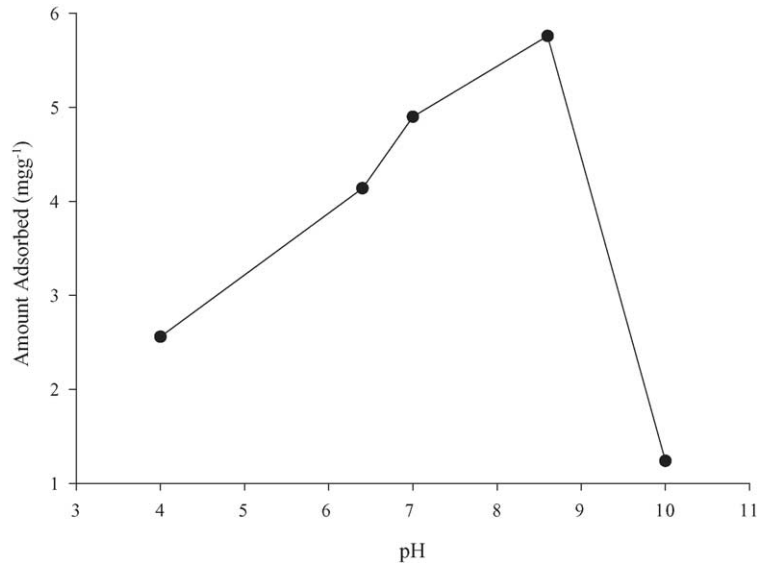
Fig. 7. Effect of pH on the removal of Cd(II) by adsorption on rice polish. Conditions: concentration, $125\,\text{mg}\,\text{l}^{-1}$; particle size, $178\,\mu\text{m}$; temperature, $30\,^{\circ}\text{C}$; agitation rate, 125 rpm.

3.7. Empirical model

In order to find out the rate of removal of Cd(II) from wastewater by rice polish, the following empirical mathematical model was developed between contact time (min) and initial and remaining concentration C_0 and C_t (both in $\text{mg}\,\text{l}^{-1}$) of Cd(II), respectively:

$$\log(t+1) = K(C_0 - C_t)^A \tag{10}$$

where K and A are constants. The following relations for different C_0, was developed:

For $C_0 = 100\,\text{mg}\,\text{l}^{-1}$:

$$\log(t+1) = 0.4725(C_0 - C_t)^{0.7846} \tag{11}$$

For $C_0 = 125\,\text{mg}\,\text{l}^{-1}$:

$$\log(t+1) = 0.5561(C_0 - C_t)^{0.7633} \tag{12}$$

For $C_0 = 150\,\text{mg}\,\text{l}^{-1}$:

$$\log(t+1) = 0.6072(C_0 - C_t)^{0.7469} \tag{13}$$

The values of A and K were determined from the slope and intercept of the plot $\log[\log(t+1)]$ versus $\log(C_0 - C_t)$. The plots of $\log(t+1)$ versus $(C_0 - C_t)^A$ was linear in each case suggested the applicability of the above model.

The log–log plot of K and C_0 produces a straight line having the following relationship:

$$K = 0.0865 C_0^{0.7689} \tag{14}$$

The plot of A and C_0 also gives straight line having the following relationship:

$$A = 0.8591 - 0.0008 C_0 \tag{15}$$

The applicability of the proposed model is helpful to calculate the amount of Cd(II) adsorbed.

3.8. Multiple regression analysis

We have seen the effect of initial adsorbate concentration, contact time, temperature and pH of the system on Cd(II) removal by rice polish. The cumulative effect of all these independent variables (cadmium removal) are given by the following relation:

$$Y = 2.2436 + 0.5880a_1 + 0.4646a_2 - 0.6023a_3$$
$$+ 0.3772a_4 + 0.0841a_5 \tag{16}$$

where Y is the predicted value of Cd(II) removal; a_1 the concentration of adsorbate; a_2 the contact time; a_3 the

Table 5
Percentage removal at different conditions on experimental and predicted values at equilibrium time, pH 8.6 and agitation rate 125 rpm

Initial adsorbate concentration ($\text{mg}\,\text{l}^{-1}$)	Percentage removal		Temperature (°C)	Percentage removal	
	Exp. value	Predicted value		Exp. value	Predicted value
100	96.80	98.54	20	96.48	95.40
125	92.16	90.59	30	92.16	90.59
150	85.87	85.29	40	86.60	85.78

temperature; a_4 the pH; a_5 the agitation rate of the system. The model values calculated with the help of Eq. (16) and the experimental values are given in Table 5. It may be seen that predicted values are pretty close to the experimental values. From these results it is concluded that all independent variables have cumulative effect on the cadmium removal by rice polish.

4. Conclusion

Rice polish has been found to be a very effective biosorbent for the removal of Cd(II) from wastewater. The maximum removal of cadmium(II) was found to be 9.72 mg g^{-1} at pH 8.6, initial Cd(II) concentration of 125 mg l^{-1} and temperature of 20 °C. The removal of cadmium was rapid in initial stages and became slower afterwards; it was also confirmed by mass transfer studies. The double nature of the curves were attributed to the fact that the adsorption in the initial stages was due to the boundary layer diffusion whereas in the later stages adsorption was due to the intraparticle diffusion. Thermodynamic studies confirm that the process was spontaneous and exothermic. The fit of the adsorption data into Langmuir isotherm confirmed the monolayer adsorption.

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