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The adsorption of Cd(II) ions on sulphuric acid-treated wheat bran

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Abstract

The adsorption of Cd(II) ions which is one of the most important toxic metals by using sulphuric acid-treated wheat bran (STWB) was investigated. The effects of solution pH and temperature, contact time and initial Cd(II) concentration on the adsorption yield were studied. The equilibrium time for the adsorption process was determined as 4 h. The adsorbent used in this study gave the highest adsorption capacity at around pH 5.4. At this pH, adsorption capacity for an initial Cd(II) ions concentration of 100 mg/L was found to be 43.1 mg/g at 25 °C for contact time of 4 h. The equilibrium data were analysed using Langmuir and Freundlich isotherm models to calculate isotherm constants. The maximum adsorption capacity (q_{max}) which is a Langmuir constant decreased from 101.0 to 62.5 mg/g with increasing temperature from 25 to 70 °C. Langmuir isotherm data were evaluated to determine the thermodynamic parameters for the adsorption process. The enthalpy change (ΔH°) for the process was found to be exothermic. The free energy change (ΔG°) showed that the process was feasible. The kinetic results indicated that the adsorption process of Cd(II) ions by STWB followed first-order rate expression and adsorption rate constant was calculated as 0.0081 l/min at 25 °C. It was observed that the desorption yield of Cd(II) was highly pH dependent.

Keywords: Wheat bran; Sulphuric acid; Adsorption; Cd(II) ions

1. Introduction

The presence of toxic metals in the environment can be harmful to humans and living species even in low concentration. Since toxic metals do not degrade into harmless end-products, they can accumulate in living bodies and getting concentrated through the food chain [1]. Cadmium is the one of the toxic metals and has received a great deal of attention. It is accumulated in the human body, causing erothrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity [2]. The main source of cadmium in wastewaters is discharging of waste stream from metallurgical alloying, ceramics, metal plating, photograph, pigment works, textile printing industries, lead mining and sewage sludge [3]. The conventional methods that have been used to reduce cadmium content of wastewaters include its precipitation as hydroxide and carbonate.

Precipitations methods are costly and can create secondary problems with metal-bearing sludge. Adsorption is the other method that can be used for heavy metals removal from wastewaters, in which activated carbon is one of the most recommended adsorbents. Since commercial activated carbons are too expensive for large-scale use, the methods for removing heavy metals from wastewaters have resulted in the search for the development of alternatives from cheaper and readily available materials that may be useful to reduce the pollutant content to the levels established by the legislation. Therefore, the usage of low-cost adsorbents in the adsorption studies carried out in recent years is becoming widespread. Some of the low-cost adsorbents reported for the removal of cadmium are aerobic granular sludge [4] marina alge *Padina* sp. [5] and *Durvillaea potatorum* [6], low-grade phosphate [7], Turkish fly ash [8], hazelnut shell [9], perlite [10], *Pinus pinaster* bark [11], crab shell [12], bone char [13], sugar beet pulp [14], *C. vulgaris* [15], tree fern [16] and waste tea [17].

Wheat bran is a by-product of wheat milling industries, which is a widely available and abundant natural material. In our previous studies, we used wheat bran dehydrated with concentrated sulphuric acid as an adsorbents to remove Cr(VI) [18] and Cu(II) ions [19] from aqueous solutions. The aim of this study was to investigate adsorption capability of wheat bran treated with sulphuric in the removing process of Cd(II) ions from

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aqueous media. The adsorption experiments were carried out in a batch system and the influence of contact time, pH, initial Cd(II) ion concentration and temperature were investigated on the adsorption yield of Cd(II) ions. The adsorption equilibrium was analysed using Langmuir and Freundlich models and some thermodynamic and kinetic parameters were calculated for the adsorption process.

2. Materials and methods

2.1. Adsorbent

The wheat bran provided from a local market in Elazığ, Turkey, was ground and sieved. Preparation of sulphuric acid-treated wheat bran (STWB) used as adsorbent was carried out by treating one part of wheat bran sieved to under 50 mesh and two parts (by weight) of concentrated sulphuric acid (w/w, 98%) for 24 h. To remove the excess sulphuric acid, dehydrated wheat bran were washed with distilled water until the pH of supernatants remained constant at around 4.0. After the treated wheat bran with sulphuric acid has been dried at 105 °C for 24 h, dried samples were ground and sieved to obtain the size of 50 mesh fractions. This fraction was stored in polyethylene bag and used in the experiments carried out in this study.

2.2. Preparation of solutions

Stock solution of Cd(II) ions with a concentration of 1000 mg/L were prepared from analytical reagent grade $3CdSO_4{\cdot}8H_2O$ supplied by Reidel-de Haen Chemicals. Working solutions of Cd(II) ions were prepared by diluting the stock solution. The pHs of solutions were adjusted to the required value by using 0.1 M NaOH or 0.1 M HNO_3 solution. Distilled water was used for the preparations of all solutions and dilutions.

2.3. Adsorption experiments

All adsorption experiments were performed on a mechanical shaker equipped with a thermostatic water bath at 150 rpm using a 100 mL capped plastic flask. To investigate the effect pH and contact times, 0.1 g STWB was mixed with 50 mL Cd(II) solutions of 100 mg/L at different pHs and 25 °C in the plastic flasks for contact times ranging from 2 to 8 h. In the experiments related to kinetic studies, contact period was varied from 15 min up to equilibrium time (4 h). In preparation of working solutions, an aliquot amount of stock solution was added to a conical flask of 50 mL and diluted with distilled water and NaOH or HCl solutions to obtain different concentration of Cd(II) solution and pHs. This solution was transferred to the plastic flask (150 mL) containing 0.1 g STWB. At the end of predetermined contact time the final pH of mixture was measured and recorded as pH_f. Since the preparation of adsorbent was made with concentrated sulphuric acid, the value of initial pH of the mixture cannot be correctly recorded because of remaining acid. For that reason, the final pH of mixture was considered as a variable. For isotherm studies, a series of flasks containing 50 mL Cd(II) solutions in the range of 50–500 mg/L were prepared. The weighed amount of 0.1 g STWB was added to each flask and the mixtures were agitated at constant temperature of 25, 40, 50, 60 and 70 °C. These experiments were carried out at a constant pH of 5.4 ± 0.2 for a contact period of 4 h. Desorption studies were conducted by shaking 0.1 g STWB containing 4.31 mg Cd(II) ions with 50 mL distilled water at 25 °C and different pH values for 4 h.

In adsorption and desorption studies, at the end of the required contact period, the aqueous phase was separated from adsorbent by centrifugation at 5000 rpm for 10 min. Cd(II) concentration in filtrates were analysed by an atomic absorption spectrophotometer (Perkin Elmer 370 model). The adsorption percentage of Cd(II) ions was calculated by the difference of initial and final concentration using the equation expressed as follows.

$$\text{Adsorption yield}\,(\%) = \frac{(C_o - C_t)V}{C_o} \times 100 \quad (1)$$

The adsorption capacity of Cd(II) ions adsorbed per gram adsorbent (mg/g) was calculated using

$$q = \frac{(C_o - C_t)V}{W} \quad (2)$$

where C_o and C_t are the initial and at any time (t) concentration (mg/L) of Cd(II) ions in the solution, V the volume (L) of solution and W is the weight (g) of the adsorbent. For the equilibrium conditions in these equations, C_e (equilibrium concentration) and q_e (adsorbed metal ions at equilibrium) must be written instead of C_t and q. C_e and q_e have the same unit with C_t and q, respectively.

3. Results and discussion

3.1. Effect of pH

The influence of pH on Cd(II) removal by adsorption on sulphuric acid-treated wheat bran was studied at varying pH values for different contact times, and the results are shown in Fig. 1. It is clear that adsorption capacity is very low at strong acidic medium. This has been noticed by several workers [20–22]. The

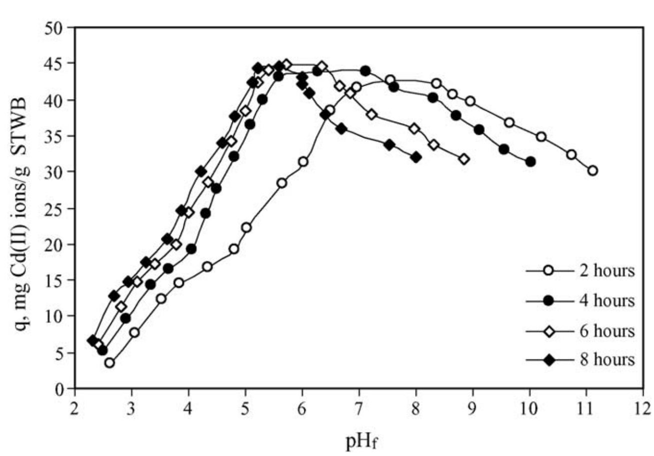

Fig. 1. Effect of pH and contact time on the adsorption of Cd(II) ions by STWB. (*Conditions:* 0.1 g STWB, 50 mL 100 mg/L Cd(II) solution, contact temperature: 25 °C.)

lower adsorption capacity observed at low pHs may be explained on the basis on electrostatic repulsion forces between positively charged H_3O^+ and Cd^{2+} ions. At low pH values, the concentration of H_3O^+ is higher than that of Cd(II) ions and, hence, these ions are adsorbed on the active sites of activated adsorbents, leaving Cd(II) ions free in the solution. When pH increased, Cd(II) ions would replace with H_3O^+ ions competing effect of which decreased depending upon the increase of the pH, which increased the adsorption yield of the Cd(II) ions. The adsorption capacity increases with increase in pH value up to 5.0–6.0 for contact times 4, 6 and 8 h. In the experiments that contact times was applied 2 h, increase trend in the adsorption capacity depending upon final pH of solution is lower. For this condition, adsorption capacity attained a maximum value at around pH of 7.0. As seen from Fig. 1, there are no important differences among maximum adsorption capacities corresponding to contact times of 4, 6 and 8 h. This means that 4 h is a sufficient time for adsorption equilibrium. For that reason, the contact time was applied as 4 h in the subsequent experiments and optimum pH was selected as 5.4 ± 0.2. The optimum pH for Cd(II) ions adsorption by carbon from hazelnut shell treated with sulphuric acid was observed in the pH range from 4.0 to 6.0 [9]. In another work carried out by activated carbons from almond shells, olive and peach stone, optimum pH has been reported as 5.0 [23]. Mohan and Singh [2] have reported optimum pH as 4.5 for Cd(II) adsorption on activated carbon from bagasse. In other studies carried out by activated carbon from sugar beet pulp [21], Gridih coal [24], activated carbon from sugar beet pulp impregnated with phosphoric acid [25] spent grain [20], the optimum pH were 6.3, 6.6, 6.3 and 5.3–5.6, respectively. The differences in these results may be due to the aqueous medium employed in their studies. At final pH of 5.4 ± 0.2, the adsorption capacity was determined as 43.1 mg/g at the end of contact time of 4 h, which corresponds a removal yield of 86.2%. Above pH 7.0 the removal takes place by adsorption as well as precipitation of Cd(II) ions in the form of $Cd(OH)_2$. The decrease in adsorption yield at alkaline conditions can be attributed the formation of $Cd(OH)_3{}^-$ ions taking place as a result of dissolution $Cd(OH)_2$ due to its amphoter characteristic. The hydrolysis and precipitation of metal ions affect adsorption by changing the concentration and form of soluble metal species those are available for adsorption. The hydrolysis of Cd(II) ions may be represented by following reaction [26].

$$Cd^{2+} + 2nH_2O \Leftrightarrow Cd(OH)_n{}^{2-n} + nH_3O^+ \quad (3)$$

Depending upon the pH of the solution, various species of cadmium can be formed during the hydrolysis. The hydrolysis extend of Cd(II) ions is unimportant up to approximately pH 7.5 and cadmium are in the form of Cd^{2+} ions at this pH. For that reason it can be said that the adsorption mechanisms can be explained on the basis of H_3O^+–Cd^{2+} exchange reaction.

3.2. Adsorption isotherms

The analysis of equilibrium data to construct adsorption isotherms is usually important for design of adsorption systems. Adsorption isotherms express the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at a constant temperature. The adsorption data have been analysed with two adsorption models, which are Langmuir and Freundlich isotherm equations.

3.2.1. Langmuir isotherm

Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of adsorbent, which is a most important parameter for an adsorption system. Langmuir equation may be written as:

$$q_e = \frac{q_{max} K C_e}{1 + K C_e} \quad (4)$$

The above equation can be rewritten to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K q_{max}} + \frac{C_e}{q_{max}} \quad (5)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L) in solution, q_e the amount adsorbed per unit mass of adsorbent (mg/g). The constant q_{max} is the maximum adsorption capacity and has the same unit with q_e. K (L/mg) is a constant related to the affinity of binding sites or bonding energy. q_{max} denotes a practical limiting adsorption capacity when the surface of adsorbent is completely covered with adsorbate. A plot of C_e/q_e versus C_e should be a straight line with a slope $1/q_{max}$ and intercepts $1/Kq_{max}$ (Fig. 2).

The Langmuir constants (q_{max} and K) calculated from the plots in Fig. 2 are presented in Table 1. The data related to the equilibrium obeyed well the Langmuir models. As seen from the values of regression coefficients presented in Table 1, the values of those are higher than 0.992. The values of q_{max} and K calculated from Langmuir plots were found to be 101.0 mg/g and 0.051 L/mg for the experiments carried out at 25 °C. The values of both q_{max} and K decreased with a rise in the solution temperature. The values of q_{max} decreased from 101.0 to 62.5 mg/g, when the solution temperature increased from 25 to 70 °C. The decreasing trend was observed for the values of K

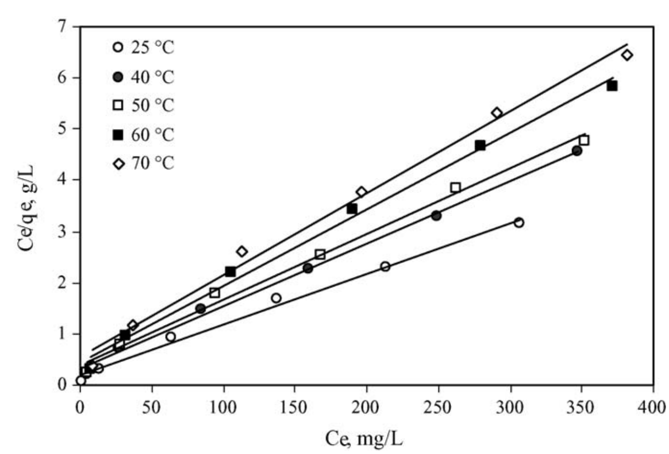

Fig. 2. The linearized Langmuir adsorption isotherms for Cd(II) adsorption by STWB. (*Conditions:* 0.1 g STWB, 50 mL 100 mg/L Cd(II) solution at various concentration, final pH: 5.4 ± 0.2, contact time: 240 min.)

Table 1
Langmuir and Freundlich constants for adsorption of Cd(II) ions on STWB

Temperature (°C)	Langmuir constants			Freundlich constants		
	q_{max} (mg/g)	K (L/mg)	R^2	K_f	n	R^2
25	101.0	0.051	0.992	21.77	3.75	0.998
40	82.0	0.039	0.996	14.76	3.41	0.986
50	78.1	0.034	0.993	13.91	3.44	0.993
60	67.1	0.032	0.993	13.00	3.66	0.998
70	62.5	0.030	0.992	11.97	3.69	0.998

depending upon the temperature of solution. The decrease in the values of q_{max} and K with temperature indicates that the Cd(II) ions are favourably adsorbed by STWB at lower temperatures, which shows that the adsorption of Cd(II) ions by STWB is exothermic.

The effect of isotherm shape has been considered to predict on whether an adsorption system is favourable or unfavourable. The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_L, which is defined by the following relationship [27]:

$$K_L = \frac{1}{1 + KC_o} \tag{6}$$

where K is the Langmuir constant and C_o is the initial concentration Cd(II) ions. R_L value indicates the shape of isotherm. If K_L value is between 0 and 1, the adsorption process is favourable. If $K_L > 1$ the process is unfavourable. When the value of K_L is equal to 0 adsorption process is irreversible. If K_L is equal to 1 the process is linear. The K_L values were found to be less than 1 and greater than 0 (Table 2) for all experiments carried out at different initial concentrations and temperatures. The values of K_L at 25 °C for adsorption of Cd(II) ions by STWB decreased from 0.282 to 0.038 while the initial concentration of Cd(II) concentration increased from 50 to 500 mg/L. Similar trend was observed for the other results that carried out at different temperatures. These results show that Cd(II) ions adsorption on STWB is more favourable at the higher Cd(II) concentration.

3.2.2. *Freundlich isotherm*

The empirical Freundlich isotherm is based on adsorption on a heterogeneous surface and express by the following equation:

$$q_e = K_f C_e^{1/n} \tag{7}$$

Table 2
The values of K_L based on the Langmuir isotherm for adsorption of Cd(II) ions on STWB

Co (mg/L)	Temperature (°C)				
	25	40	50	60	70
50	0.282	0.339	0.370	0.384	0.400
100	0.164	0.205	0.227	0.238	0.250
200	0.089	0.114	0.128	0.135	0.143
300	0.061	0.079	0.089	0.094	0.100
400	0.047	0.060	0.074	0.072	0.077
500	0.038	0.049	0.056	0.059	0.062

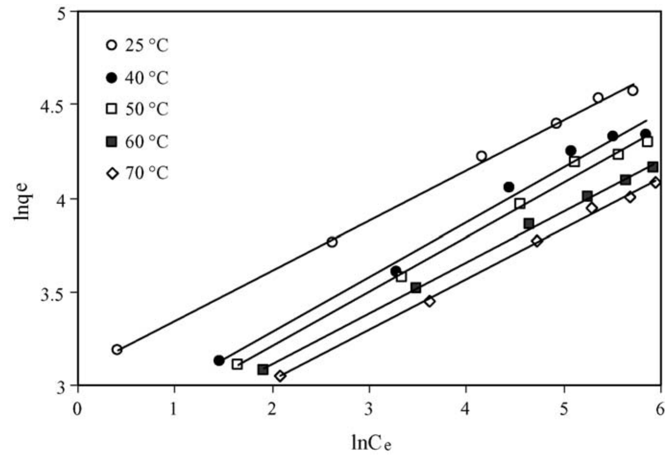

Fig. 3. The linearized Freundlich adsorption isotherms for Cd(II) adsorption by STWB. (*Conditions:* 0.1 g STWB, 50 mL 100 mg/L Cd(II) solution at various concentration, final pH: 5.4 ± 0.2, contact time: 240 min.)

where K_f and n are the Freundlich constants related to adsorption capacity and intensity, respectively. Eq. (7) is generally used in the linear form, represented by

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{8}$$

Fig. 3 shows the experimental data fitted to linear form of Freundlich isotherm for Cd(II) ions adsorption by STWB. The values of K_f and n were determined from the plot shown in Fig. 3 and also listed in Table 1.

The values of K_f decreased from 21.77 to 11.97 with the rising temperature of solution from 25 to 70 °C. K_f is a measure of adsorption capacity and the decrease in the values of it with temperature confirms that the adsorption process of Cd(II) ions by STWB is exothermic. In all experiments that were carried out at different temperatures, the values of n were higher than 3 and did not show an outstanding changes with temperature. Reed and Matsumoto [26] have pointed out that the situation $n > 1$ is most common and may be due to a distribution of surface sites or any factor that cause a decrease in adsorbent–adsorbate interaction with increasing surface density. According to McKay et al. [28] the values of n in the range of 2–10 represent good adsorption.

In conclusion, sulphuric acid-treated wheat bran has a good affinity for Cd(II) ions and its adsorption capacity decreased with the increasing temperature of solution.

3.3. *Thermodynamic parameters*

The thermodynamic parameters, namely free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$), have an important role to determine spontaneity and heat change for the adsorption process. Equilibrium constant can be used to evaluate the thermodynamic parameters.

The very useful relationship between standard free energy change and equilibrium constant is given by the following equation:

$$\Delta G^\circ = -RT \ln K \tag{9}$$

Table 3
Free energy change for the adsorption of Cd(II) on STWB

Temperature (°C)	$-\Delta G^\circ$ (kJ/mol)	K (L/mol)
25	21.45	5732.9
40	21.83	4384.0
50	22.16	3821.9
60	22.68	3597.1
70	23.18	3372.3

where K is the adsorption equilibrium constant obtained from Langmuir isotherms, ΔG° the free energy change, R the universal gas constant, 8.314 J/mol K and T is the absolute temperature. The free energy change calculated for the adsorption of Cd(II) ions by STWB at each temperature studied are shown in Table 3. The values of ΔG° calculated at different temperatures are negative. The negative values of ΔG° indicate that the adsorption process is spontaneous with high preference of Cd(II) ions for STWB.

The van't Hoff equation is used to determine the value of the equilibrium constant with temperature changes. The equation is

$$\frac{\mathrm{d}(\ln K)}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2} \quad (10)$$

Integrated form of this equation can be represented as follows:

$$-\ln K = \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + C \quad (11)$$

where C is a constant. Multiplying both sides of Eq. (11) by RT, Eq. (12) can be obtained.

$$-RT \ln K = \Delta H^\circ + RTC \quad (12)$$

If RTC term is replaced with $-T\Delta S^\circ$ and Eq. (9) combined with Eq. (12), expression (13) can be obtained.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

The enthalpy and entropy changes of the process can be determined from the slope and intercept of line obtained by plotting free energy change, ΔG°, versus temperature T. This plot was found to be linear (Fig. 4). The enthalpy change, ΔH°, and entropy change, ΔS°, for this process were calculated as −9.84 kJ/mol and 38.60 J/mol K, respectively. The negative value of ΔH° shows that this process is exothermic and Cd(II) ions is adsorbed more efficiently on STWB at lower temperatures. The entropy change with positive sign reflects the affinity of STWB for Cd(II) ions in the treated solution and suggests that both enthalpy and entropy are responsible for making the ΔG° negative. Positive entropy change is possibly stemming from the changes take place in structure of adsorbent and dispersing of water molecules from Cd(II) ions surrounded by water molecules during adsorption process.

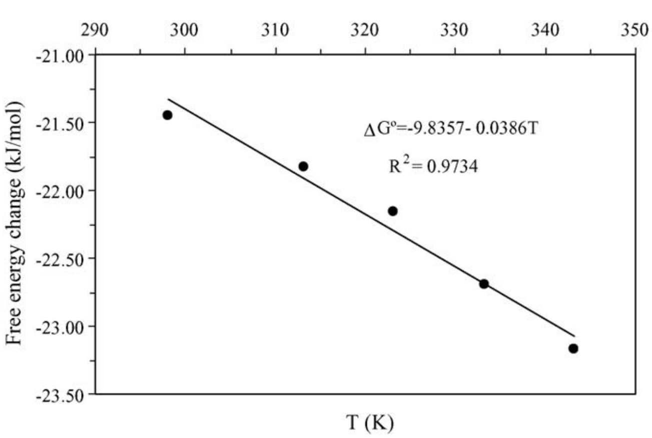

Fig. 4. Plot of free energy change (ΔG°) vs. temperature.

3.4. Kinetic study

In practice, to design an adsorption reactor it is necessary to determine adsorption rate constant due to adsorption process is time dependent. The rate constant for Cd(II) adsorption on STWB was determined using the model given by Lagergren for the adsorption of liquid/solid system. It was pointed out that Lagergren model was known as first order kinetic model and based on the solid capacity [29]. This model is generally expressed as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{\mathrm{ad}}(q_\mathrm{e} - q_t) \quad (14)$$

where q_e and q_t (both in mg/g) are the amount of adsorbate per amount of adsorbent at equilibrium and at any time t, respectively. k_{ad} (l/min) is the rate constant of pseudo first-order adsorption. After integrating of Eq. (14) applying the boundary conditions $t = 0$–t and $q_t = 0$–q, it becomes:

$$\log(q_\mathrm{e} - q_t) = \log(q_\mathrm{e}) - \frac{k_{\mathrm{ad}}}{2.303}t \quad (15)$$

The plot of $\log(q_\mathrm{e} - q_t)$ versus t gives a straight line as can be seen in Fig. 5. The first-order rate constant (k_{ad}) was calculated from the slope of the plot as 0.0081 l/min. In ideal conditions, the theoretical q_e value calculated from the intercept of Lagergren plot should be equal to the experimental value of q_e. The experimental value of q_e employed in this study is 43.1 mg/g. The theoretical value of q_e obtained from the intercept of Lagergren plot (Fig. 5) was found to be 35.1 mg/g. There are certain

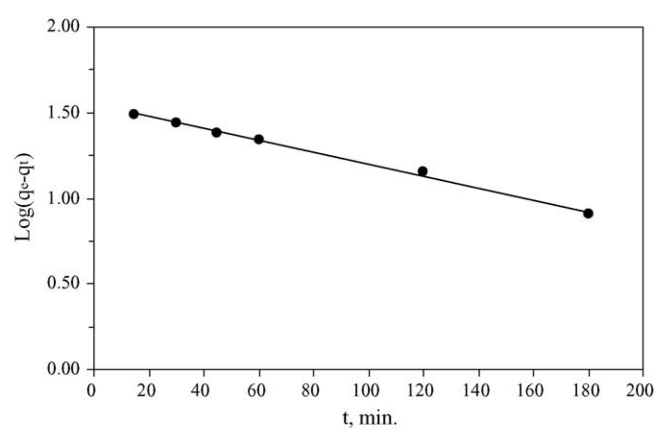

Fig. 5. Plot of $\log(q_\mathrm{e} - q_t)$ vs. time for the rate constants of the adsorption process. (*Conditions:* 50 mL 100 mg/L Cd(II) solution; 0.1 g STWB; final pH: 5.4 ± 0.2; temperature: 25 °C.)

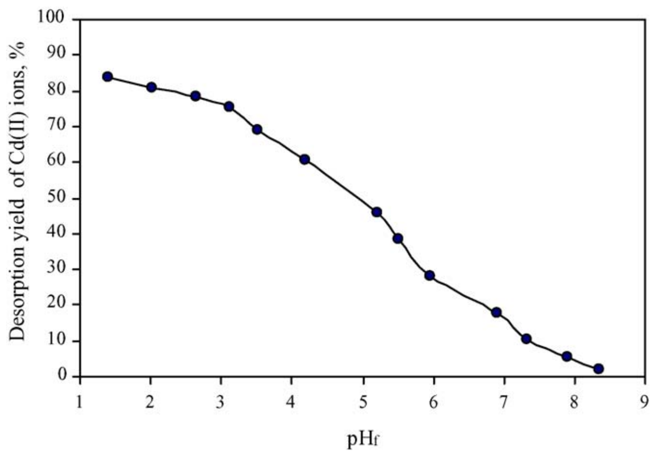

Fig. 6. Desorption yield of Cd(II) ions depending upon final pH of solution. (*Conditions:* 50 mL distilled water; 0.1 g STWB containing 4.31 mg Cd(II) ions; temperature: 25 °C.)

differences between the experimental value of q_e and theoretical value of q_e. However, the correlation coefficient for the first-order kinetic model was found to be 0.9954. This shows that there is a significant linear relationship between kinetic data and first order rate expression of Lagergren.

3.5. Desorption studies

The desorption of Cd(II) ions were investigated depending upon pH of solution. The results are shown in Fig. 6. These results were obtained by contacting 0.1 g STWB impregnated with 4.31 mg Cd(II) ions with 50 mL distilled water has different pH values for 4 h at 25 °C. As seen from Fig. 6, desorption yield of Cd(II) ions is, to a large extent, pH dependent. The percentage of Cd(II) ions desorbed from STWB impregnated with adsorbate was found to be approximately 84% at pH 1.40, thereafter it sharply decrease towards strong alkaline region. At very strong acidic conditions Cd(II) ions were desorbed effectively due to replacing Cd^{2+} ions adsorbed on the adsorbent site with H_3O^+ ions adding to the solution to make medium acidic. The desorption yield of Cd(II) ions is very high at strong acidic conditions confirms that the adsorption mechanisms of Cd(II) ions by sulphuric acid-treated wheat bran (STWB) is based on the exchange of Cd^{2+} with H_3O^+ during desorption.

4. Conclusions

Based upon the experimental results of this study, the following conclusions can be drawn:

1. It was observed that the removal yield increased with increasing contact time and reached the equilibrium state within 4 h.
2. The adsorption process is highly pH dependent and the optimum pH was determined as 5.4 ± 0.2. At this pH, the removal yield of Cd(II) ions was found to be 86.2%.
3. The results related to adsorption isotherms showed that the equilibrium data fitted very well to the Langmuir and Freundlich model. It was observed that the isotherm constant decreased with increasing temperature. The values of q_{max} decreased from 101.0 to 62.5 mg/g, when the solution temperature increased from 25 to 70 °C, which shows the adsorption process is exothermic.
4. The enthalpy (ΔH°) and entropy change (ΔS°) were calculated as −9.84 kJ/mol and 38.60 J/mol K for the process. Negative values of enthalpy change indicate the exothermic nature of the adsorption process. Free energy change (ΔG°) with negative sign reflects the feasibility and spontaneous nature of the process.
5. The kinetic analysis of the study showed that the adsorption of Cd(II) ions onto STWB could be described well with the first-order kinetic model and the rate constant for the process was found to be 0.0081 l/min at 25 °C.
6. It was observed that the desorption yield of Cd(II) ions is very high at strong acidic medium.

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