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Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran

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Abstract

Studies on a batch sorption process using wheat bran as a low cost sorbent was investigated to remove cadmium ions from aqueous solution. The influence of operational conditions such as contact time, cadmium initial concentration, sorbent mass, temperature, solution initial pH, agitation speed and ionic strength on the sorption kinetics of cadmium was studied. Pseudo-second-order model was evaluated using the six linear forms as well as the non-linear curve fitting analysis method. Modeling of kinetic results shows that sorption process is best described by the pseudo-second-order model using the non-linear method. The sorption of cadmium was found to be dependent on initial concentration, sorbent mass, solution pH, agitation speed, temperature, ionic strength and contact time. The value of activation energy (12.38 kJ mol^{-1}) indicates that sorption has a low potential barrier corresponding to a physical process. Sorption equilibrium isotherms at different temperatures was determined and correlated with common isotherm equations such as Langmuir and Freundlich models. It was found that the Langmuir model appears to well fit the isotherm data but a worse correlation was obtained by the Freundlich model. The five Langmuir linear equations as well as the non-linear curve fitting analysis method were discussed. Results show that the non-linear method may be a better way to obtain the Langmuir parameters. Thermodynamic parameters such as ΔH°, ΔS° and ΔG° were calculated. These parameters indicate that the sorption of cadmium by wheat bran is a spontaneous process and physical in nature involving weak forces of attraction and is also endothermic.

Keywords: Sorption; Cadmium; Wheat bran; Langmuir isotherm; Pseudo-second-order model; Linear analysis; Non-linear analysis

1. Introduction

Heavy metals released by a number of industrial processes in the environment are some of the major pollutants of soil and water resources. The concentration of these pollutants must be reduced to meet ever increasing legislative standards and recovered where feasible.

Various physicochemical techniques for removing metal ions from wastewaters include chemical precipitation, adsorption, ion exchange, extraction and membrane processes. Chemical precipitation is the most common utilized conventional technique. Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater and water supplies [1,2]. Activated carbon is the most common used adsorbent, however, it is relatively expensive.

Biosorption technology, utilizing natural materials or industrial and agricultural wastes to remove cadmium from aqueous media, offers an efficient and cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques. Since the cost of this processes are rather expensive, the use of agricultural residues or industrial by-product have been studied for years and many references on this topic can be found in the literature. Recently, application of a number of agricultural materials such as modified cellulosic material [3], bagasse sugar [4], sawdust [5], rice husk [6], spent grain [7], pine bark [8], rice polish [9], tree fern [10], modified corn cobs [11], apple residues [12], hazelnut shell [13], coconut husk [14], etc., have been reported for the removal of cadmium from aqueous solutions. Biosorption is a rapid, reversible, economical and ecofriendly technology in contrast to traditional methods used for removal of heavy metals from

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Nomenclature

b	Langmuir constant related to the free energy of sorption ($L\,mg^{-1}$)
b_M	Langmuir constant related to the free energy of sorption ($L\,mol^{-1}$)
C_0	the initial concentration of the solute in the bulk solution ($mg\,L^{-1}$)
C_e	the equilibrium concentration of the solute in the bulk solution ($mg\,L^{-1}$)
ΔG°	Gibb's free energy change ($kJ\,mol^{-1}$)
h	initial sorption rate ($mg\,g^{-1}\,min^{-1}$)
ΔH°	enthalpy change ($J\,mol^{-1}$)
K_1	Lagergren pseudo-first-order rate constant (min^{-1})
K_2	the pseudo-second-order rate constant ($g\,mg^{-1}\,min^{-1}$)
K_F	Freundlich constant indicative of the relative sorption capacity of the sorbent ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)
n	Freundlich constant indicative of the intensity of the sorption
q	the amount of solute sorbed at any time t ($mg\,g^{-1}$)
q_e	the amount of solute sorbed per unit weight of sorbent at equilibrium ($mg\,g^{-1}$)
q_m	the maximum sorption capacity ($mg\,g^{-1}$)
R^2	Coefficient of determination
R_g	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
R_L	dimensionless separation factor of Hall
ΔS°	entropy change ($J\,mol^{-1}\,K^{-1}$)
t	time (min)
T	temperature (K)

aqueous streams [15,16]. Biosorption can be defined as the ability of biological materials to accumulate heavy metals through metabolically mediated or physicochemical pathways of uptake [17].

Therefore, there is a need for the search of low cost and easily available biomaterials, which can sorb cadmium. The aim of this work is to study the sorption characteristics of wheat bran, an abundant and inexpensive natural material, towards cadmium ions from aqueous solutions. Many researchers have studied the removal of heavy metals by natural and modified wheat bran [18–23]. However, in these studies, modeling of metal ions sorption data by various models (kinetics and isotherms) was carried out using linear regression analysis. In the present investigation, linear least-squares method and non-linear regression analysis method of the widely used equations in the filed of sorption (pseudo-second-order kinetic model and Langmuir and Freundlich isotherms) were compared in an experiment examining cadmium ion sorption by natural wheat bran. Additionally, effects of some operating conditions for the sorption of cadmium by natural wheat bran such as sorbent mass, agitation speed and ionic strength were not previously studied.

2. Materials and methods

2.1. Sorbate and sorbent

Cadmium solutions of desired concentration have been prepared by dissolving the appropriate amount of its sulfate ($3CdSO_4 \cdot 8H_2O$, Fluka) in distilled water. All chemicals used in this study were of analytical grade.

The bran of wheat was obtained from a market as solid waste and was used for sorption experiments without any treatment. The wheat bran was sieved repeatedly, in order to eliminate wheat semolina, non-wheat bran solids and fine particles of the material, and dried to constant weight. Finally, the sorbent material is screened to eliminate fine particles (<0.5 mm) and stored in a vacuum desiccator before use.

2.2. Dynamics

The initial concentration of cadmium solution was $100\,mg\,L^{-1}$ for all experiments, except for those carried out to examine the effect of the initial concentration of cadmium. For kinetic studies, the batch method was used because of its simplicity. For cadmium removal kinetic experiments, 2 g of wheat bran was contacted with 0.5 L of cadmium solution in a beaker of 1 L agitated vigorously by a mechanic stirrer using a water bath maintained at a constant temperature. The stirring speed was kept constant at 400 rpm. At predetermined intervals of time, samples of the mixture was withdrawn at suitable time intervals, and filtered through a paper filter. These were analyzed by atomic absorption spectrometry (Perkin-Elmer A310) for the concentration of cadmium.

The experiments were performed at the pH that resulted from solving the metal in water (around 5) without further adjustment, except for those carried out to examine the effect of the solution pH.

All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported. The maximum standard deviation was ±2%.

2.3. Equilibrium isotherms

Equilibrium isotherms were determined by contacting a fixed mass of wheat bran (2 g) with 500 mL of cadmium solutions in beakers. A range of cadmium concentrations ($25–300\,mg\,L^{-1}$) was tested. A series of such beakers was then agitated at a constant speed of 400 rpm in a water bath with temperatures 20, 30 and 40 °C, respectively. After agitating the beakers for 2 h, the reaction mixtures were filtered through filter paper, and then the filtrates was analyzed for the remaining cadmium concentration with atomic absorption spectrometry (Perkin-Elmer A310). The experiments were performed at pH 5, which resulted from dissolution of cadmium sulfate in distilled water without further adjustment.

All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported. The maximum standard deviation was ±2%.

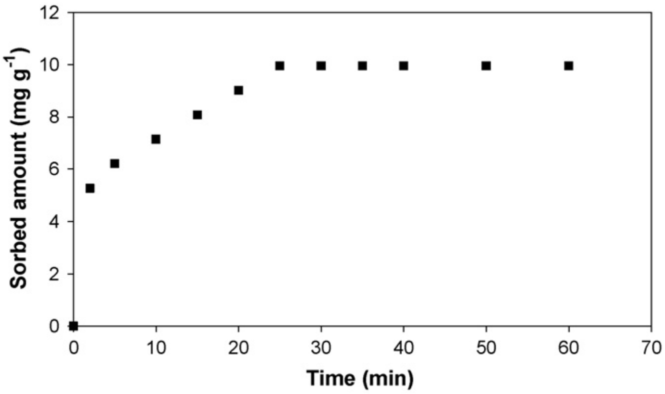

Fig. 1. Effect of contact time on the sorption of cadmium by wheat bran.

3. Results and discussion

3.1. Sorption dynamics

3.1.1. Effect of contact time

The rate of metal ion removal is of great significance for developing sorbent-based water technology. The necessary contact time to reach the equilibrium depends on the initial cadmium concentration and the sorption capacity increases with the initial metal concentration in all cases. Sorption isotherms are usually determined under equilibrium conditions. A series of contact time experiments has been carried out with a constant initial cadmium concentration of 100 mg L^{-1}, temperature of 20 °C and constant stirrer speed of 400 rpm. The effect of contact time on the sorption of cadmium ions by wheat bran is shown in Fig. 1. As seen from this figure, the contact time necessary to reach equilibrium is about 25 min and the amount of cadmium sorbed by wheat bran increases with time and, at some point in time, reaches a constant value beyond which no more is removed from solution. At this point, the sorbed amount of cadmium by wheat bran is in a state of dynamic equilibrium with the amount of the cadmium desorbing from the sorbent. The time required to attain this state of equilibrium of metal at the equilibrium time reflects the sorption capacity of the sorbent under the operating conditions.

Dynamics of cadmium sorption by wheat bran can be modeled by the pseudo-first-order Lagergren equation and the pseudo-second-order model.

The pseudo-first-order equation (Eq. (1)) and the pseudo-second-order expression (Eq. (2)) are given by

$$\ln(q_e - q) = \ln q_e - K_1 t \quad (1)$$

$$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (2)$$

where K_1 is the pseudo-first-order rate constant (min^{-1}), q_e the amount of cadmium sorbed at equilibrium (mg g^{-1}), q the amount of cadmium on the surface of wheat bran at any time, t (mg g^{-1}), t the time (min) and K_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

The pseudo-second-order equation can be linearized to six different linear forms as shown in Table 1. Expression of type 6 was previously reported by Blanchard et al. [24] for the exchange reaction of divalent metallic ions onto NH_4^+ ions fixed onto zeolite particles. A type 1 expression as shown in Table 5 was previously reported by Ho [25,26]. This is the most used linearized form for the pseudo-second-order equation.

The initial sorption rate h (mg g^{-1} min^{-1}) is given by the following equation

$$h = K_2 q_e^2 \quad (3)$$

The pseudo-first-order kinetic constant K_1 (min^{-1}) and the amount of cadmium sorbed at equilibrium q_e (mg g^{-1}) based on pseudo-first-order kinetics can be obtained from the plot of $\ln(q_e - q)$ versus t. The lower coefficient of determination value and the amount of cadmium sorbed at equilibrium determined using this model (Table 2) suggest that it is inappropriate to use this equation to represent the sorption of cadmium by wheat bran.

Linear regression analysis using the six linear expressions of the pseudo-second-order equation was used to determine the model parameters for the sorption of cadmium by wheat bran. The obtained results are shown in Table 2. It was observed that the rate constant, the sorbed amount at equilibrium and the initial sorption rate values obtained from the six linear forms of pseudo-second-order expressions were different. It is clear that transformations of non-linear pseudo-second-order kinetic model to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least-squares method. The very higher coefficient of determination value for type 1 expression suggests that the pseudo-second-order kinetic expression is the optimum kinetic expression to represent the uptake of cadmium by wheat bran. Additionally, a type 1 pseudo-second-order expression predicts reasonably the theoretical q_e value. The lower determination coefficient values for types 2–6 pseudo-second-order expressions suggest that it is not appropriate to use these types of linearization.

Table 1
Linear forms of the pseudo-second-order kinetic model

Type	Linear form	Plot	Parameters
Type 1	$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	t/q vs. t	q_e = 1/slope; K_2 = slope^2/intercept; h = 1/intercept
Type 2	$\frac{1}{q} = \frac{1}{q_e} + \frac{1}{K_2 q_e^2} \frac{1}{t}$	$1/q$ vs. $1/t$	q_e = 1/intercept; K_2 = intercept^2/slope; h = 1/slope
Type 3	$q = q_e - \frac{1}{K_2 q_e} \frac{q}{t}$	q vs. q/t	q_e = intercept; $K_2 = -1$/(slope × intercept); $h = -$intercept/slope
Type 4	$\frac{q}{t} = K_2 q_e^2 - K_2 q_e q$	q/t vs. q	$q_e = -$intercept/slope; K_2 = slope^2/intercept; h = intercept
Type 5	$\frac{1}{t} = -K_2 q_e + K_2 q_e^2 \frac{1}{q}$	$1/t$ vs. $1/q$	$q_e = -$slope/intercept; K_2 = intercept^2/slope; h = slope
Type 6	$\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t$	$1/(q_e - q)$ vs. t	q_e = 1/intercept; K_2 = slope; h = slope/intercept^2

Table 2
Pseudo-second-order kinetic parameters obtained by using the linear and non-linear methods

Type	Parameters	Values
Type 1	K_2 (g mg^{-1} min^{-1})	28.71×10^{-3}
	q_e (mg g^{-1})	10.65
	h (mg g^{-1} min^{-1})	3.26
	R^2	0.997
Type 2	K_2 (g mg^{-1} min^{-1})	51.46×10^{-3}
	q_e (mg g^{-1})	9.87
	h (mg g^{-1} min^{-1})	5.02
	R^2	0.871
Type 3	K_2 (g mg^{-1} min^{-1})	46.2×10^{-3}
	q_e (mg g^{-1})	10.08
	h (mg g^{-1} min^{-1})	4.69
	R^2	0.793
Type 4	K_2 (g mg^{-1} min^{-1})	35.37×10^{-3}
	q_e (mg g^{-1})	10.44
	h (mg g^{-1} min^{-1})	3.86
	R^2	0.793
Type 5	K_2 (g mg^{-1} min^{-1})	42.26×10^{-3}
	q_e (mg g^{-1})	10.17
	h (mg g^{-1} min^{-1})	4.37
	R^2	0.871
Type 6	K_2 (g mg^{-1} min^{-1})	41.6×10^{-3}
	q_e (mg g^{-1})	16.34
	h (mg g^{-1} min^{-1})	11.11
	R^2	0.877
Non-linear	K_2 (g mg^{-1} min^{-1})	31.83×10^{-3}
	q_e (mg g^{-1})	10.51
	h (mg g^{-1} min^{-1})	3.52
	R^2	0.968
Lagergren	K_1 (min^{-1})	10.02×10^{-3}
	q_e (mg g^{-1})	7.36
	R^2	0.936

Additionally, the sorption uptake kinetics for cadmium by wheat bran was analyzed by non-linear curve fitting analysis method, using Microcal(TM) Origin® software, to fit the pseudo-second-order equation (Table 2). The pseudo-second-order model constants obtained from the non-linear and linear methods differed even when compared with the results of type 1 expression, which had the highest coefficient of determination (Table 1). It seems that the best fit was obtained by the expression of Ho (type 1) as compared with other linear expressions because it had the highest coefficient of determination and because the model parameters were closer to those obtained using the non-linear method. Thus, it will be more appropriate to use non-linear method to estimate the parameters involved in the kinetic equation.

3.1.2. Effect of initial concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of solutes between the aqueous and solid phases. The effect of initial cadmium concentration on the rate of sorption is shown in Fig. 2. From Fig. 2, it was observed that the metal removal varied with varying initial cadmium concentration. It was observed that metal sorption

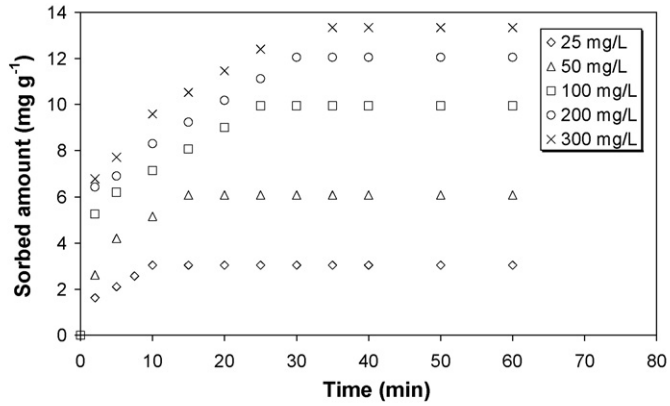

Fig. 2. Effect of initial concentration of metal on the sorption of cadmium by wheat bran.

occurred rapidly. The sorption efficiency of cadmium increased gradually with increasing contact time and reached a plateau afterward. An increase in initial cadmium concentration leads to an increase in the sorption capacity of cadmium by wheat bran. Equilibrium uptake increased with the increasing of initial metal ions concentration at the range of experimental concentration. The initial rate of sorption was greater for higher initial cadmium concentration, because the resistance to the metal uptake decreased as the mass transfer driving force increased.

For initial concentrations of 100 and 200 mg L^{-1}, the ability of wheat bran to sorb maximum amount of cadmium within, respectively, 25 and 30 min indicates that it is an effective biosorbent for the removal of cadmium from wastewater. When initial cadmium concentration was increased from 25 to 300 mg L^{-1}, the equilibrium sorption capacity increased from 3.04 to 13.34 mg g^{-1}.

Table 3 shows the pseudo-second-order kinetic parameters for different initial concentrations of cadmium obtained utilizing the non-linear curve fitting analysis method. The sorption of cadmium by wheat bran for different solute initial concentrations was found to be adequately represented by the pseudo-second-order kinetic model. Increasing the initial metal concentration enhanced both the initial sorption rate and theoretical amount sorbed at equilibrium. Conversely, the pseudo-second-order rate constant decreased with initial cadmium concentration.

3.1.3. Effect of sorbent mass

The effect of a variation of sorbent mass on the dynamics of sorption of cadmium by wheat bran is reported in Fig. 3. The sorption of cadmium increases with an increase in sorbent amount. This may be attributed to increased sorbent surface area and availability of more sorption sites resulting from the increased mass of the sorbent. But amount of metal sorbed per unit mass of sorbent decreases with an increase in sorbent amount. At higher wheat bran to solute concentration ratios, there is a very fast superficial sorption onto the sorbent surface that produces a lower solute concentration in the solution than when the biomaterial to solute concentration ratio is lower. This is because a fixed mass of wheat bran can only sorb a certain amount of metal. Therefore, the higher the sorbent dosage is, the larger the volume of effluent that a fixed mass of biosorbent

Table 3
Pseudo-second-order kinetic parameters obtained by using the non-linear method for different initial cadmium concentrations

Parameters	25 mg L^{-1}	50 mg L^{-1}	100 mg L^{-1}	200 mg L^{-1}	300 mg L^{-1}
K_2 (g mg^{-1} min^{-1})	85.91×10^{-3}	55.55×10^{-3}	31.83×10^{-3}	22.91×10^{-3}	21.28×10^{-3}
q_e (mg g^{-1})	3.75	6.62	10.51	12.64	13.94
h (mg g^{-1} min^{-1})	1.21	2.43	3.52	3.66	4.14
R^2	0.980	0.989	0.968	0.950	0.969

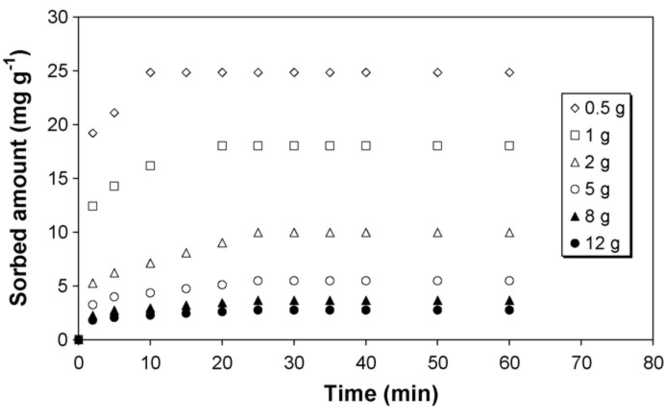

Fig. 3. Effect of sorbent dose on the sorption of cadmium by wheat bran.

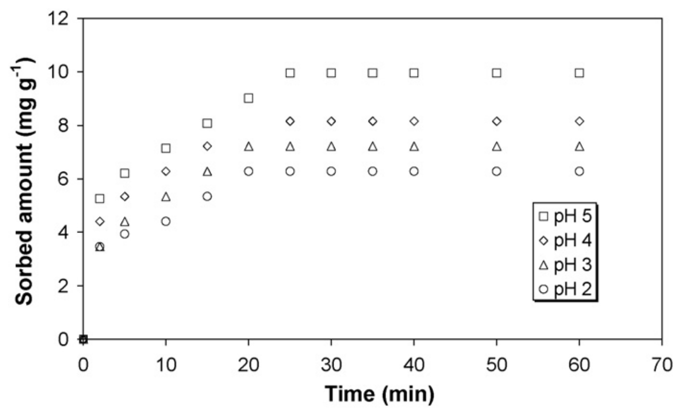

Fig. 4. Effect of solution initial pH on the sorption of cadmium by wheat bran.

can purify is. The decrease in amount of cadmium sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent. Thus, with increasing sorbent mass, the amount of cadmium sorbed onto unit weight of sorbent gets reduced, thus causing a decrease in sorption capacity with increasing sorbent mass concentration.

The experimental dynamic data were modeled by the pseudo-second-order equation using the non-linear curve fitting analysis method. The determined parameters of the model are shown in Table 4. The removal of cadmium by wheat bran can be sufficiently represented by the pseudo-second-order kinetic equation. The theoretical amount sorbed at equilibrium decreases from 25.43 to 2.8 mg g^{-1} when the sorbent mass increases from 0.5 to 12 g, respectively. The initial sorption rate decreased with the increase in the mass of sorbent.

3.1.4. *Effect of solution initial pH*

The pH value of the metal solution plays an important role in the whole sorption process and particularly on the sorption capacity. Any sorbent surface creates positive or negative charge on its surface. This charge is proportional to the pH of the solution, which surrounds the sorbent particles. In order to study, the effect of this parameter on the metal sorption by wheat bran, solution initial pH was varied within the range 2–5. This pH range was chosen in order to avoid metal solid hydroxide precipitation. The effect of solution initial pH on the sorption dynamics for cadmium onto wheat bran is shown in Fig. 4. This figure depicts that the pH significantly affects the extent of sorption of cadmium by wheat bran and the cadmium sorption amount increases from 6.28 to 9.95 mg g^{-1} when the solution pH increases from 2 to 5. The variation in the removal of cadmium by wheat bran with respect to pH can be elucidated by considering the surface charge of the sorbent materials and the speciation of cadmium(II). According to the Cd(II) speciation diagram [27], Cd^{2+} is the predominant ionic species at pH ≤ 6. The minimal sorption amount obtained at low pH is partly due to the fact that protons are strong competing sorbate because of their higher concentration and high mobility and partly to the fact that the solution pH influences the sorbent surface charge. The surface charge of the wheat bran is positive at pH < PZC, is neutral at pH = PZC, and is negative at pH > PZC. At pH > PZC, the Cd^{2+} ions in solution are attracted to the surface of sorbent, thus favoring sorption. At higher pH values, the lower number of protons and greater number of negative charges results in greater cadmium sorption. The effect of pH on the sorption kinetics is attributed to electrostatic attraction existing between the wheat bran surface and the Cd^{2+} ions in solution.

Table 4
Pseudo-second-order kinetic parameters obtained by using the non-linear method for different sorbent mass

Parameters	0.5 g	1 g	2 g	5 g	8 g	12 g
K_2 (g mg^{-1} min^{-1})	57.09×10^{-3}	47.76×10^{-3}	31.83×10^{-3}	95.1×10^{-3}	162.29×10^{-3}	250.82×10^{-3}
q_e (mg g^{-1})	25.43	18.53	10.51	5.64	3.74	2.8
h (mg g^{-1} min^{-1})	36.92	16.40	3.52	3.03	2.27	1.97
R^2	0.994	0.994	0.968	0.984	0.984	0.983

Table 5
Pseudo-second-order kinetic parameters obtained by using the non-linear method for different solution pH

Parameters	pH 2	pH 3	pH 4	pH 5
K_2 (g mg^{-1} min^{-1})	54.05×10^{-3}	39.34×10^{-3}	46.24×10^{-3}	31.83×10^{-3}
q_e (mg g^{-1})	6.67	7.82	8.65	10.51
h (mg g^{-1} min^{-1})	2.4	2.41	3.46	3.52
R^2	0.96	0.98	0.981	0.968

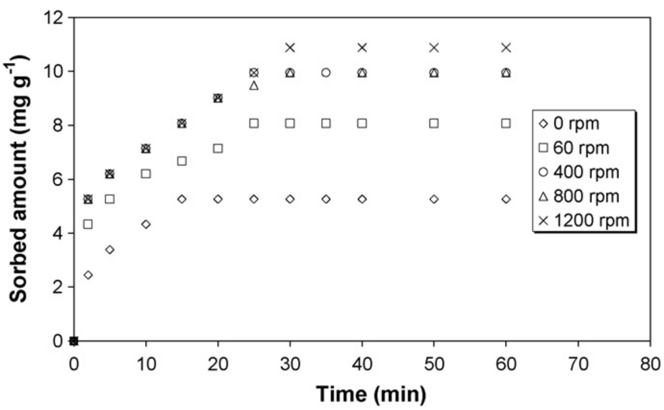

Fig. 5. Effect of agitation speed on the sorption of cadmium by wheat bran.

The sorption dynamics of cadmium by wheat bran for different solution pH were fitted by the pseudo-second-order model using the non-linear curve fitting analysis method. The determined kinetic parameters are given in Table 5. The sorption of cadmium using wheat bran was found to be well described by the pseudo-second-order kinetic model. Increasing the initial metal solution pH enhanced both the initial sorption rate and theoretical amount sorbed at equilibrium.

3.1.5. Effect of stirring speed

The effect of stirring speed on the removal of cadmium by wheat bran at different stirring speeds, ranging from 0 (no stirring) to 1200 rpm, is shown in Fig. 5. The data shown in Fig. 5 indicates that the difference of sorption rate was significant as the stirring speed increases.

The amount of cadmium sorption increases with the increase of the stirring speed from 0 to 400 rpm. When increasing the stirring speed, the diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding sorbent particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. The change in sorption rate was insignificant as the stirring speed increases from 400 to 800 rpm. For a stirring speed of 1200 rpm, a higher sorbed amount at equilibrium was obtained. This can be explained by the decrease of the sorbent particle size that affects the sorption capacity.

The sorption dynamic data for cadmium by wheat bran at different stirring speeds was analyzed by the non-linear curve fitting analysis method to fit the pseudo-second-order kinetic equation. Table 6 shows the kinetic parameters obtained using the non-linear curve fitting analysis method. Increasing the stirring speed enhanced both the initial sorption rate and theoretical amount sorbed at equilibrium. However, the pseudo-second-order rate constant decreased with the stirring speed.

3.1.6. Effect of ionic strength

In water, salt is present in a wide range of concentrations depending on the source and the quality of the water. The presence of salt or co-ions in solution can affect the sorption of metal ions. The effect of salt concentration (ionic strength) on the amount of cadmium sorbed by wheat bran was analyzed over the NaCl concentration range from 0 to 20 g L^{-1}. The effect of ionic strength on sorption rate of cadmium by wheat bran is presented in Fig. 6. As seen in Fig. 6, the presence of NaCl significantly influences the sorption rate of cadmium. The metal sorption decreases with increasing NaCl concentration. This behavior could be attributed to the competitive effect between cadmium ions and cations from the salt (Na^+) for the sites available for the sorption process. Additionally, salt screens the electrostatic interaction between sorbent and sorbate and the great ionic strength influences on the activity coefficient of cadmium, which should decrease the sorbed amount with an increase of NaCl concentration.

The experimental results for different NaCl concentrations were modeled by the pseudo-second-order equation using the non-linear curve fitting analysis method. The determined parameters of the model are given in Table 7. The sorption of cadmium by wheat bran was found to be well represented by the pseudo-second-order kinetic equation. The pseudo-second-order kinetic constant, initial sorption rate and theoretical amount sorbed at equilibrium decreased with the increase in ionic strength.

Table 6
Pseudo-second-order kinetic parameters obtained by using the non-linear method for different agitation speeds

Parameters	0 rpm	60 rpm	400 rpm	800 rpm	1200 rpm
K_2 (g mg^{-1} min^{-1})	62.72×10^{-3}	45.5×10^{-3}	31.83×10^{-3}	32.38×10^{-3}	20.48×10^{-3}
q_e (mg g^{-1})	5.72	8.44	10.51	10.44	11.62
h (mg g^{-1} min^{-1})	2.05	3.24	3.52	3.53	2.77
R^2	0.985	0.977	0.968	0.970	0.953

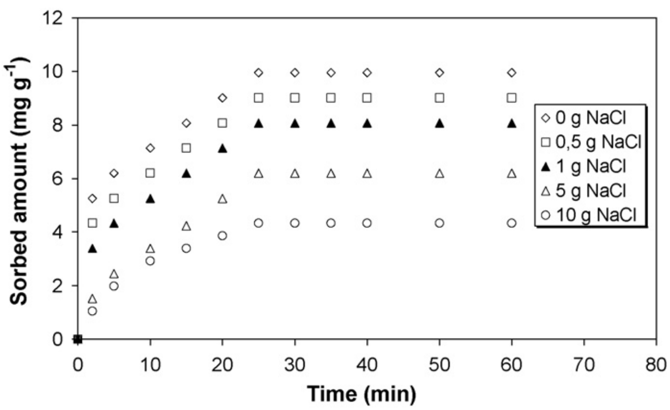

Fig. 6. Effect of ionic strength on the sorption of cadmium by wheat bran.

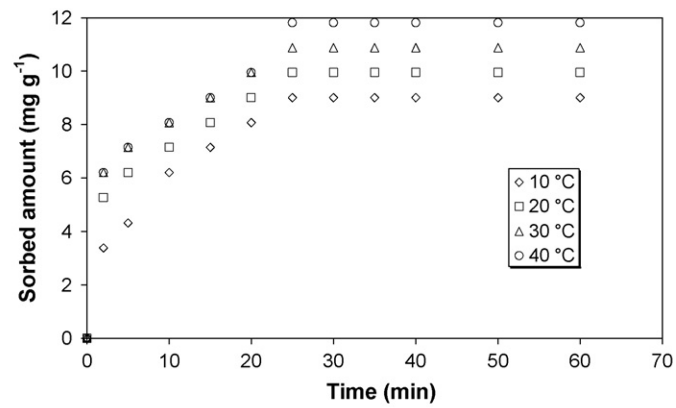

Fig. 7. Effect of temperature on the sorption of cadmium by wheat bran.

3.1.7. Effect of temperature

The temperature has two major effects on the sorption process. Increasing the temperature is known to increase the rate of diffusion of the sorbate, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the sorbent for a particular sorbate. In this phase of study, a series of experiments were conducted at 10, 20, 30 and 40 °C to investigate the effect of temperature on the sorption dynamics. Fig. 7 depicts the effect of contact time on the sorption dynamics of cadmium by wheat bran at four different temperatures. The measurement of kinetics of the process at different temperatures exhibits an increase in the cadmium removal with the increase in temperature. The result again confirms endothermic nature of the process. Additionally, the present results show that by increasing temperature from 10 to 40 °C the necessary time to reach equilibrium does not change.

The dynamic results were correlated with the pseudo-second-order rate equation by using the non-linear curve fitting analysis method and the obtained parameters are listed in Table 8. The theoretical amount sorbed at equilibrium, pseudo-second-order kinetic constant and initial sorption rate increased with the increase in temperature.

Arrhenius equation for pseudo-second-order kinetic model is given as follows:

$$K_2 = A_0 \exp\left(-\frac{E_a}{R_g T}\right) \quad (4)$$

where A_0 is the temperature independent factor (g mg^{-1} min^{-1}), E_a the activation energy of sorption (kJ mol^{-1}), R_g the gas constant (8.314 J mol^{-1} K^{-1}) and T is the solution temperature (K). The slope of plot of $\ln K_2$ versus $1/T$ is used to evaluate the activation energy (Fig. 8). The magnitude of activation energy gives an idea about the type of sorption, which is mainly physical or chemical. Low activation energies (5–40 kJ mol^{-1}) are characteristics for physisorption, while higher activation energies (40–800 kJ mol^{-1}) suggest chemisorption [28]. The obtained result (12.38 kJ mol^{-1}) for the sorption of cadmium by wheat bran indicates that the sorption has a potential barrier and corresponds to a physisorption.

3.2. Equilibrium isotherms

Sorption equilibrium isotherms are basic requirements for designing any sorption system. The sorption isotherm indicates how the sorbate distributes between the liquid phase and the

Table 7
Pseudo-second-order kinetic parameters obtained by using the non-linear method for different ionic strength

Parameters	0 g NaCl	0.5 g NaCl	1 g NaCl	5 g NaCl	10 g NaCl
K_2 (g mg^{-1} min^{-1})	31.83×10^{-3}	26.96×10^{-3}	21.95×10^{-3}	12.49×10^{-3}	26.79×10^{-3}
q_e (mg g^{-1})	10.51	9.73	9	7.78	5.14
h (mg g^{-1} min^{-1})	3.52	2.55	1.78	0.76	0.71
R^2	0.968	0.986	0.971	0.974	0.988

Table 8
Pseudo-second-order kinetic parameters obtained by using the non-linear method for different temperatures

Parameters	10 °C	20 °C	30 °C	40 °C
K_2 (g mg^{-1} min^{-1})	17.17×10^{-3}	31.83×10^{-3}	43.7×10^{-3}	52.6×10^{-3}
q_e (mg g^{-1})	10.27	10.51	11.11	11.46
h (mg g^{-1} min^{-1})	1.81	3.52	5.39	6.91
R^2	0.982	0.968	0.966	0.916

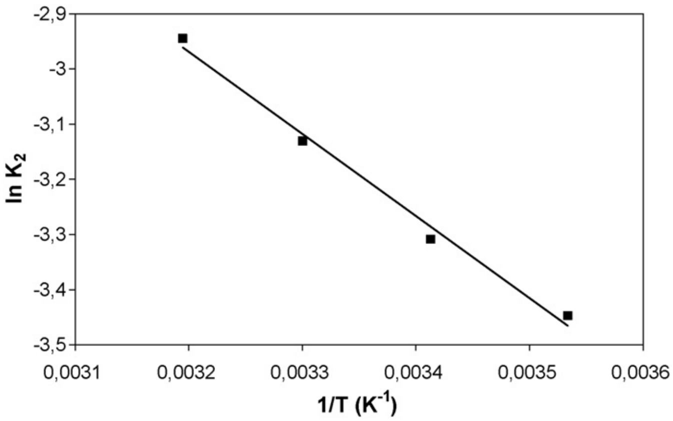

Fig. 8. Plot of $\ln K_2$ vs. reciprocal temperature for the sorption of cadmium by wheat bran.

solid phase when the sorption process reaches an equilibrium state. Fig. 9 presents the amount of cadmium sorbed at 20, 30 and 40 °C plotted against its concentration in aqueous phase at equilibrium. Isotherm data obtained with a range of initial cadmium concentration showed an increase in the amount of cadmium sorbed when the initial metal concentration was raised from 25 to 300 mg L^{-1}. Additionally, the amount of metal sorbed increased following an increase in temperature from 20 to 40 °C. The shape of the curves clearly indicated that the isotherms for all temperatures belong to L-type according to the classification of equilibrium isotherm in solution by Giles et al. [29].

Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of sorption process as a unit operation. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes. In the present investigation, the equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. Linear regression is frequently used to determine the best-fitting isotherm, and the method of least squares has been used for finding the parameters of the isotherms. However, the Langmuir isotherm can be linearized as five different types (Table 9). The more-popular linear forms used are Langmuir-1 and Langmuir-2. The linear form of the Freundlich model is also shown in Table 9.

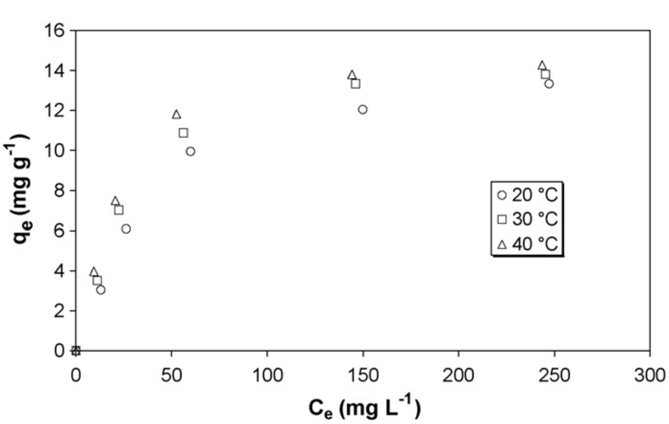

Fig. 9. Equilibrium isotherms of cadmium sorption by wheat bran at different temperatures.

Table 9
Freundlich and Langmuir isotherms and their linear forms

Isotherm		Linear form	Plot
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ vs. $\ln C_e$
Langmuir-1		$\frac{1}{q_e} = \frac{1}{bq_m}\frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs. $1/C_e$
Langmuir-2	$q_e = \frac{q_m b C_e}{1+bC_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b}$	C_e/q_e vs. C_e
Langmuir-3		$q_e = -\frac{1}{b}\frac{q_e}{C_e} + q_m$	q_e vs. q_e/C_e
Langmuir-4		$\frac{q_e}{C_e} = -bq_e + bq_m$	q_e/C_e vs. q_e
Langmuir-5		$\frac{1}{C_e} = bq_m \frac{1}{q_e} - b$	$1/C_e$ vs. $1/q_e$

The sorption data for cadmium by wheat bran at different temperatures were analyzed by a linear regression analysis to fit the Freundlich and the five linearized expressions of Langmuir isotherm models. The details of these different forms of linearized Langmuir equations and the method to estimate the Langmuir constants q_m and b from these plots were explained in Table 9. Out of the five different types of linearized Langmuir isotherm equations, Langmuir-1 and Langmuir-2 are the most frequently used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution. Values of the Langmuir constants and the Freundlich parameters are presented in Table 10 for the sorption of cadmium by wheat bran at 20, 30 and 40 °C. The linear analysis using different linear forms of the Langmuir equation will significantly affect calculations of the Langmuir parameters. The values of the coefficient of determination obtained from Langmuir-2 expression indicate that there is strong positive evidence that the sorption of cadmium by the biosorbent follows the Langmuir isotherm.

Table 10
Parameters of the Langmuir and Freundlich isotherms obtained using the linear method

Isotherm		T (°C)		
		20	30	40
Langmuir-1	b (L mg^{-1}) × 10^3	14.56	21.01	31.62
	q_m (mg g^{-1})	19.61	19.08	17.76
	R^2	0.983	0.978	0.992
Langmuir-2	b (L mg^{-1}) × 10^3	22.14	32.83	44.32
	q_m (mg g^{-1})	15.82	15.72	15.75
	R^2	0.995	0.996	0.998
Langmuir-3	b (L mg^{-1}) × 10^3	20.68	28.9	37.31
	q_m (mg g^{-1})	16.28	16.4	16.54
	R^2	0.887	0.894	0.948
Langmuir-4	b (L mg^{-1}) × 10^3	18.3	25.8	35.4
	q_m (mg g^{-1})	17.26	17.21	16.02
	R^2	0.887	0.894	0.948
Langmuir-5	b (L mg^{-1}) × 10^3	13.8	19.9	31.1
	q_m (mg g^{-1})	20.33	19.71	17.91
	R^2	0.983	0.978	0.992
Freundlich	n	2.09	2.37	2.65
	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	1.11	1.6	2.11
	R^2	0.901	0.88	0.882

Table 11
Parameters of the Langmuir and Freundlich isotherms obtained using the non-linear method and thermodynamic parameters

Isotherm		T (°C)		
		20	30	40
Langmuir	b (L mg^{-1}) × 10^3	23.85	33	42.68
	q_m (mg g^{-1})	15.71	15.94	16.05
	R^2	0.992	0.993	0.994
	$\Delta G°$ (kJ mol^{-1})	−19.23	−20.70	−22.06
	$\Delta H°$ (kJ mol^{-1})	22.17		
	$\Delta S°$ (J mol^{-1} K^{-1})	−141.3		
Freundlich	n	3.04	2.65	3.38
	K_F (mg$^{1-1/n}$L$^{1/n}$g^{-1})	2.44	1.77	3.03
	R^2	0.946	0.955	0.944

Additionally, the equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set experimental data. The calculated Freundlich isotherm constants and the corresponding coefficient of determination values were shown in Table 10. From Table 10, the five linear expressions of Langmuir equation were more suitable for the experimental data than was the Freundlich isotherm because the values of the coefficient of determination using the linear expressions of Langmuir are higher than that calculated utilizing the Freundlich model. This suggests that Langmuir-2 isotherm could be well represented the experimental sorption data, while a worse fit of the equilibrium isotherms is obtained using the Freundlich equation.

On the other hand, the sorption equilibrium isotherms for cadmium by wheat bran was analyzed by non-linear curve fitting analysis method, using Microcal(TM) Origin® software, to fit both the Langmuir and Freundlich models. Table 11 shows the isotherm parameters obtained using the non-linear method. The Langmuir model constants obtained from the non-linear and linear methods are different. It seems that the best fit was obtained by the Langmuir-2 expression as compared with other linear expressions because it had the highest coefficient of determination and because the model parameters were closer to those obtained using the non-linear method. The parameters of the Freundlich equation determined by linear and non-linear analysis are different. Moreover, the obtained results indicate that the Langmuir model gave an acceptable fit to the experimental data than the Freundlich equation. Thus, it will be more appropriate to use non-linear method to estimate the parameters involved in the isotherm equation.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L, given by Hall et al. [30]:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where b is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration of cadmium (mg L^{-1}).

The parameter R_L indicated the shape of isotherm as follows: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible.

The calculated R_L values, determined using Langmuir constants obtained by non-linear method, versus initial solute concentration at four different temperatures were shown in Table 12. From Table 12, it was observed that at all temperature conditions, sorption was found to be more favorable at higher concentrations. Also the value of R_L in the range of 0–1 at all initial metal ions concentrations and all the solution temperatures confirms the favorable uptake of cadmium.

3.2.1. Thermodynamic parameters

For designing sorption systems, the designer should be able to understand the changes that can be expected to occur and how fast will they take place. The fast of the reaction can be calculated from the knowledge of kinetic studies. But the changes in reaction that can be expected during the process require the brief idea of thermodynamic parameters.

Based on fundamental thermodynamic concepts, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change ($\Delta G°$) is the basic criterion of spontaneity, and a negative value indicates the reaction to be spontaneous. By using the equilibrium constant (b_M) obtained for each temperature from the Langmuir model using the non-linear method (Table 11), $\Delta G°$ can be calculated according to Eq. (6).

$$\Delta G° = -R_g T \ln b_M \tag{6}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{7}$$

A plot of $\Delta G°$ obtained using the Langmuir equilibrium constants versus temperature was found to be linear (Fig. 10). The values of $\Delta H°$ and $\Delta S°$ were, respectively, determined from the slope and intercept of the plot. The thermodynamic parameter, $\Delta G°$, is shown in Table 11. $\Delta G°$ is negative and decreases with increase in temperature indicating that sorption of cadmium by wheat bran is spontaneous and spontaneity increases with the increase in temperature. From Table 11, the value of the enthalpy

Table 12
Separation factor values for cadmium sorption by wheat bran at different temperatures

T (°C)	$b \times 10^3$ (L mg^{-1})	R_L				
		25 mg L^{-1}	50 mg L^{-1}	100 mg L^{-1}	200 mg L^{-1}	300 mg L^{-1}
20	23.85	0.626	0.456	0.295	0.173	0.123
30	33	0.548	0.377	0.233	0.132	0.092
40	42.68	0.484	0.319	0.19	0.105	0.072

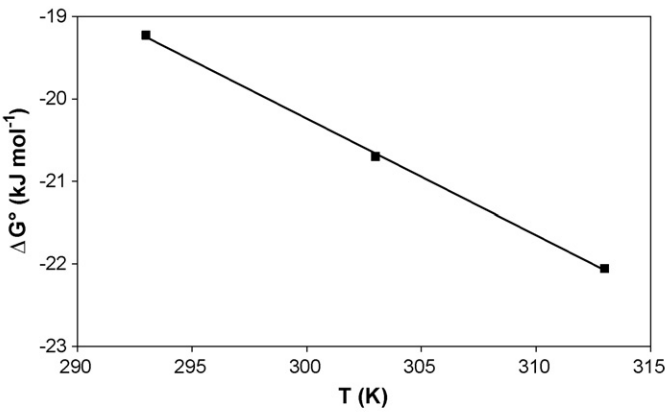

Fig. 10. Plot of Gibbs free energy change: ΔG° vs. temperature.

change ($\Delta H^{\circ} = 22.17\,\mathrm{kJ\,mol^{-1}}$) indicates that the sorption is physical in nature involving weak forces of attraction and is also endothermic, thereby demonstrating that the process is stable energetically. However, not all the cadmium biosorption systems are exothermic. Positive values of ΔH° have also reported for the biosorption of cadmium by spent grain [7], natural and oxidized corncob [31], rice husk [32] and Kraft lignin [33]. The negative entropy change (ΔS°) value ($-141.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$) corresponds to a decrease in the degree of freedom of the sorbed species.

3.3. Comparison of Cd(II) removal with different sorbents reported in literature

The sorption capacity of wheat bran for the removal of Cd(II) have been compared with those of other sorbents reported in literature and the values of sorption capacities have been summarized in Table 13. The values were reported in the form of monolayer sorption capacity. The experimental data of the present investigation show that natural wheat bran exhibits a reasonable capacity for Cd(II) sorption from aqueous solutions. This result reveals that natural wheat bran is effective sorbent for cadmium(II) ions from wastewater. It should be noted that the values and comparisons reported for cadmium removal capacity have only a relative meaning because of different testing conditions (e.g., temperature, pH, stirring speed and wastewater composition), type of biomaterials and methods.

Table 13
Comparison of monolayer sorption capacities of various biosorbents for cadmium sorption

Biosorbent	q_m (mg g^{-1})	Reference
Kraft lignin	137.14	[33]
Rice husk	103.09	[32]
Sulfuric acid-treated wheat bran	101	[19]
Grape stalk	27.88	[34]
NaOH-treated spent grain	17.3	[7]
Sugar beet pulp	17.2	[40]
Tree fern	16.3	[10]
Wheat bran	15.71	Present study
Tea-industry waste	11.29	[38]
Petiolar felt-sheath of palm	10.8	[41]
Rice polish	9.72	[9]
Sawdust of *Pinus sylvestris*	9.29	[5]
Rice husk	8.58	[6]
Pinus pinaster bark	8	[39]
Modified lignin	6.7–7.5	[3]
Corncob	6.43	[36]
Peanut hulls	5.96	[37]
Hazelnut shell	5.42	[13]
Corncob	5.09	[31]
Coconut copra meal	4.92	[35]
Exhausted coffee	1.48	[42]
Wheat bran	0.703	[18]

4. Conclusion

This study clearly suggest that the use of wheat bran as sorbent is much economical, effectual and more viable. It can be efficiently used to remove cadmium ions from aqueous solution. The different operational parameters observed during the process of investigations reveal that the contact time, initial concentration, sorbent mass, solution pH, stirring speed, ionic strength and temperature govern the overall process of sorption. The sorption process followed pseudo-second-order rate kinetics. Non-linear curve fitting analysis method was found to be the more appropriate method to determine the rate kinetic parameters. Among the six linear expressions of the pseudo-second-order kinetic model, a type 1 expression very well represent the kinetic uptake of cadmium by wheat bran. The obtained activation energy ($12.38\,\mathrm{kJ\,mol^{-1}}$) for the sorption of cadmium by wheat bran indicates that the sorption has a potential barrier and corresponds to a physisorption.

The analysis of equilibrium data shows that it is not appropriate to use the coefficient of determination of the linear regression method for comparing the best-fitting isotherm. Non-linear curve fitting analysis method was found to be the more appropriate method to determine the isotherm parameters. Langmuir-2 is the most-popular linear form which had the highest coefficient of determination compared with other Langmuir linear equations. The Freundlich isotherm gives a worse fit of the equilibrium data. The enthalpy change for the sorption process is $22.17\,\mathrm{kJ\,mol^{-1}}$, which did not indicate very strong interaction forces between cadmium ions and wheat bran. The ΔG° values were negative, which indicates that the sorption was spontaneous and the negative value of ΔS° suggests a decreased randomness at the solid/solution interface and no significant changes occur in the structure of the sorbent through the sorption of cadmium by wheat bran.

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