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Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated wheat bran

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Abstract

Sulphuric acid-treated wheat bran (STWB) was used as an adsorbent to remove Pb(II) ions from aqueous solution. It was observed that the adsorption yield of Pb(II) ions was found to be pH dependent. The equilibrium time for the process was determined as 2 h. STWB gave the highest adsorption yield at around pH 6.0. At this pH, adsorption percentage for an initial Pb(II) ions concentration of 100 mg/L was found to be 82.8 at 25 °C for contact time of 2 h. The equilibrium data obtained at different temperatures fitted to the non-linear form of Langmuir, Freundlich and Redlich–Peterson and linear form of Langmuir and Freundlich models. Isotherm constants were calculated and compared for the models used. The maximum adsorption capacity (q_{max}) which was obtained linear form of Langmuir model increased from 55.56 to 79.37 mg/g with increasing temperature from 25 to 60 °C. Similar trend was observed for other isotherm constants related to the adsorption capacity. Linear form of Langmuir isotherm data was evaluated to determine the thermodynamic parameters for the process. Thermodynamic parameters show that adsorption process of Pb(II) ions is an endothermic and more effective process at high temperatures. The pseudo *n*th order kinetic model was successfully applied to the kinetic data and the order (n) of adsorption reaction was calculated at the range from 1.711 to 1.929. The values of k_{ad} were found to be 5.82×10^{-4} and 21.81×10^{-4} $(min^{-1})(mg/g)^{1-n}$ at 25 and 60 °C, respectively. Activation energy was determined as 29.65 kJ/mol for the process. This suggest that the adsorption Pb(II) ions by STWB is chemically controlled.

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

1. Introduction

The heavy metal pollution is of greatest concern among the kinds of environmental pollution because of heavy metals' high toxicity and mobility. They do not degrade into harmless products in water sources and accumulate in living bodies and getting concentrated through the food chain [1]. The release of heavy metals from many industrial processes leads to an increase the concentration of heavy meals in aquatic system, which causes serious environmental problems in view of human health. Therefore, many studies have been conducted by researchers to reduce the concentration of heavy metals in the wastewaters before being discharged into aquatic systems. Lead is the one of the considerable metals that is among the potentially toxic heavy metals [2]. The major source of lead pollution in wastewaters is discharging of waste stream from acid battery manufacturing, metal plating and finishing, printing, metallurgical alloying, lead mining, ceramics and glass industries [3]. The presence of lead in drinking water even at low concentration may cause such diseases as anemia, encephalopathy, hepatitis and nephritic syndrome [4]. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain [5]. The removal of lead from wastewaters by traditional processes includes its precipitation with lime or alkali hydroxide, coagulation, electrolytic deposition, reverse osmosis and ion exchange. These traditional methods are costly and have significant disadvantages such as generation of metal-bearing sludge or wastes, incomplete metal removal, the disposal of secondary waste.

Adsorption is an efficient and economical method that can be used for the removal of heavy metals from wastewaters. However, the cost of adsorbents to be used is a most important restricted factor in view of applicability of adsorption process. In recent year, 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

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may be useful to reduce the pollutant content to the levels established by the legislation.

It has been observed that the majority of recent adsorption studies were conducted with activated carbon produced from uneconomical sources, various natural biosorbents and mineral adsorbents with low-cost. The use of low-cost natural biosorbents such as maize bran [6], *Pinus sylvestris* sawdust [7], maple sawdust [8], *Azadirachta indica* (neem) leaf powder [9], *Oryza sativa* L. husk (rice husk) [10], grape stalk waste [11], chitosan [12], waste fruit residues [13], peat [14], sugar beet pulp [15,16]), spent grain [17], tree fern [18], wheat bran [19], various plant leaves [20] for the removal of Pb(II) ions from aqueous solution has been reported. In the literature, there were many studies conducted with mineral materials such as bentonite [21], granular blast furnace slag [22], activated phosphate [23] and sea nodule [24] for the removal of Pb(II) by adsorption.

Wheat bran is a by-product of wheat milling industries and may be considered as a raw material to produce an effective adsorbent. We used as an adsorbent the wheat bran treated with concentrated sulphuric acid for the removing of Cr(VI) [25], Cu(II) [26] and Cd(II) [27] ions from aqueous solutions. It is observed that the wheat bran treated with sulphuric is efficient adsorbent for the removal of the metal ions mentioned above. The main objective of this work is to investigate adsorption of Pb(II) ions from aqueous solutions using sulphuric acid-treated wheat bran (STWB) as an adsorbent by batch system. The effect of solution pH, contact time, initial Pb(II) ion concentration and temperature were investigated on the adsorption efficiency of Pb(II) ions. The adsorption equilibrium were analysed for Langmuir, Freundlich and Redlich–Peterson models using linear and non-linear regression programme of Statistica 6.0 software. This software was used to determine the rate constant and order of reaction for Pb(II) adsorption on (STWB). In addition, thermodynamic parameters were determined for adsorption Pb(II) ions to explain feasibility of process.

2. Materials and methods

2.1. Adsorbent

The preparation of sulphuric acid-treated wheat bran used as adsorbent has been described in our previous studies [27].

2.2. Preparation of solutions

A stock solution of Pb(II) ions (1000 mg/L) was prepared by dissolving $Pb(NO_3)_2$ in distilled water. $Pb(NO_3)_2$ is of analytical reagent grade and supplied by Merck. The stock solution was diluted with distilled water to obtain working solutions with desired concentrations. The pHs of solutions were adjusted to the required value by using 0.1 M NaOH or 0.1 M HNO_3 solution.

2.3. Adsorption experiments

Adsorption experiments were conducted in capped plastic flasks of 150 mL on a mechanical shaker equipped with a thermostatic water bath. To investigate the effect pH and contact times, 0.1 g STWB was added to 50 mL of Pb(II) solution of 100 mg/L concentration at different pHs and 25 °C and agitated at 150 rpm 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 (120 min). To obtain desired Pb(II) ions concentration and different pHs, the working solutions were prepared by adding an aliquot amount of stock solution to a conical flask of 50 mL and than diluting with distilled water and NaOH or HNO_3 solutions. The working solutions were transferred to the plastic flasks of 150 mL containing 0.1 g STWB. The pHs of the suspensions were recorded as final pH_f at the end of predetermined contact time. Since it is difficult to measure correctly the initial pH of the suspensions due to the acidity which cannot be removed during the washing of STWB, the final pHs of mixture were considered as variable. In the experiments related to isotherm studies, a fixed amount of STWB (0.1 g) and 50 mL Pb(II) solution with various concentrations (50–500 mg/L) was placed in a 150 mL plastic flasks and agitated at constant pH (6.0 ± 0.2) and temperature of 25, 40, 50 and 60 °C for equilibrium time of 120 min.

In all experiments at the end of agitation, supernatant was separated from adsorbent by centrifugation at 5000 rpm for 10 min and analysed for its Pb(II) ions content. An atomic absorption spectrophotometer (Perkin-Elmer 370 model) was used to determine Pb(II) ions concentration in supernatants. The adsorption percentage of Pb(II) ions was calculated by the difference of initial and final concentration using the equation expressed as follow.

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

The adsorption capacity of Pb(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 initial and at any time (t) concentration (mg/L) of Pb(II) ions in 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 same unit with C_t and q, respectively.

3. Results and discussion

3.1. Effect of pH on Pb(II) ions removal

The solution pH affects the surface charge of adsorbent, the degree of ionisation and speciation of the surface function groups [16]. As hydrolysis degree of metal ions in aqueous solution is pH dependent, the pH of solutions strongly influences the speciation of metal ions. For that reason, in many studies, it has been pointed out that the solution pH was one of the most important parameters affecting adsorption yield. Fig. 1 shows the effects of final pH on the adsorption yield of Pb(II) ions by sulphuric acid-treated wheat bran.

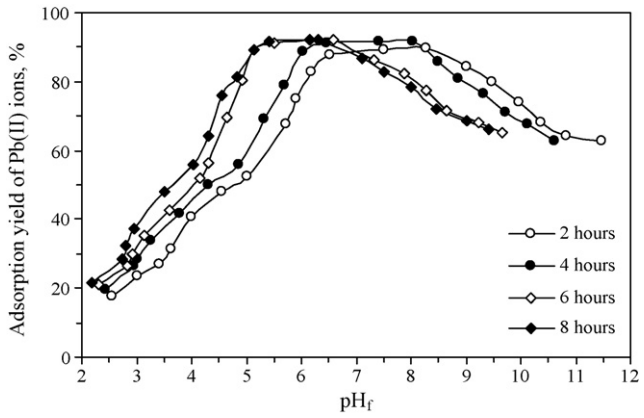

Fig. 1. Effect of pH and contact time on the adsorption of Pb(II) ions by STWB (*conditions*: 0.1 g STWB, 50 mL 100 mg/L Pb(II) solution, contact temperature: 25 °C).

It is clear that adsorption yield of Pb(II) ions increased by increasing pH of the medium up to a maximum value and thereafter the removal yield decreased. Similar trend was reported for adsorption Pb(II) ions on maize bran [6] activated carbon prepared from coconut shell [28]. This trend was observed for four plots presented in Fig. 1. There are no significant differences among removal percentage corresponding to maximum values for contact times 2, 4, 6 and 8 h. It can be said that the adsorption process attained equilibrium within 2 h. The removal yield of Pb(II) ions is very low at acidic pH values. This situation may be explained on the basis on electrostatic repulsion forces between positively charged H_3O^+ and Pb^{2+} ions. There is no precipitation at the pH lower than 6.5. The adsorption Pb(II) ions takes place on the surface of adsorbent by replacing with H_3O^+ and above pH 6.5 several hydroxide species of Pb(II) ions causes a decrease in the adsorption yield. Although maximum removal is reached at around pH 6.5, the optimum pH for the removal of Pb(II) ions on STWB was selected as 6.0 ± 0.2 at which there is no precipitation of Pb(II) ions. Singh et al. [6] have reported optimum pH as 6.5 for Pb(II) adsorption on waste maize bran. The maximum removal of Pb(II) ions by sawdust adsorption at a pH of about 5.0 [8]. In other work carried out by activated carbons prepared from almond shells, optimum pH has been reported as 4.5 [28]. Zhan and Zhao [29] have reported that the uptake of Pb(II) ions was strongly affected by solution pH and removal percentage increased sharply when solution pH rose from 2.0 to 6.0. In other study, the effect of pH was investigated in the pH range 2.0–7.0 [9]. The studies carried out by grape stalk waste [11] and chitosan [12], the optimum pH was 4.5. At final pH of 6.0 ± 0.2, the removal percentage was determined as 82.8% at the end of contact time of 2 h, which corresponds an adsorption capacity of 41.4 mg/g. It is probably that the adsorption of Pb(II) ions may be masked by precipitation of Pb(II) ions in the form of $Pb(OH)_2$ at optimum pH as a result of hydrolysis of Pb(II) ions, which cause an increase in the adsorption yield of Pb(II) ions. A decrease in adsorption was observed at alkaline conditions. The hydrolysis and precipitation of metal ions affects adsorption by changing the concentration and form of soluble metal species those are available for adsorption. In aqueous solution, the general hydrolysis reaction of Pb(II) ions may be written as following.

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

As a result of this reaction, different species of Pb(II) ion take place depending upon pH of the aqueous solution. The perusal diagram of Pb(II) speciation indicates that Pb^{2+} ions were predominant species up to pH 6.5, which was responsible for maximum adsorption [30].

3.2. Adsorption isotherms

Isotherms studies provide information on the capacity of adsorbent which is a most important parameter for an adsorption system. Adsorption isotherms are characterised by certain constants and describe the mathematical relationship between the quantity of adsorbate and concentration of adsorbate remaining in the solution at equilibrium. There are several isotherm equations describing the equilibrium and the most common of them are Langmuir, Freundlich and Redlich–Peterson models. The adsorption data have been analysed with this three adsorption models.

3.2.1. Langmuir isotherm

Langmuir adsorption isotherm is most widely used model for the adsorption process and based on monolayer coverage of adsorbate on the surface of adsorbents. According to Langmuir theory, it has been assumed that adsorption occurs at a specific homogenous site within adsorbent, each site is occupied only a adsorbate molecule, all sites are equivalent and there are no interactions between adsorbate molecules [31]. The non-linear form of Langmuir isotherm model can be represented by Eq. (3):

$$q_e = \frac{q_{max} K C_e}{1 + K C_e} \tag{3}$$

The linear form of Eq. (3) is:

$$\frac{C_e}{q_e} = \frac{1}{K q_{max}} + \frac{C_e}{q_{max}} \tag{4}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) the amount adsorbed per unit mass of adsorbent at equilibrium, q_{max} (mg/g) and K (L/mg) are the Langmuir constants related to maximum adsorption capacity and the affinity of binding sites or bonding energy for adsorption processes, respectively.

3.2.2. Freundlich isotherm

The empirical Freundlich isotherm is used to describe multi-side adsorption isotherm for heterogeneous surfaces and expressed by the following equation:

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f and n are the Freundlich constant related to adsorption capacity and intensity, respectively. Eq. (5) is generally used in

the linear form, represented by

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

3.2.3. Redlich–Peterson isotherm

Redlich–Peterson isotherm which incorporates the features of both Freundlich and Langmuir models has three-parameters known as Redlich–Peterson constants [32]. The non-linear form of the Redlich–Peterson model is expressed as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (7)$$

where A (L/g), B (L/mg)^g and C are the Redlich Peterson constants. The exponent g lies between 0 and 1. If g equals 1, Eq. (7) converts to the Langmuir form. Linear form of Eq. (7) can be described as follows:

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g \ln C_e + \ln B \quad (8)$$

To obtain the isotherm constants from the linear form of Redlich–Peterson equation, it is necessary to estimate the values of A which approaches the value of correlation coefficient to 1 by trial and error method. For that reason, the Redlich–Peterson constants for non-linear model were determined by applying regression programme of Statistica 6.0 software which uses Simlplex and Quasi-Newton estimation method based on the loss function $(q_{obs} - q_{pred})^2$ which minimizes the squares of difference between the observed and predicted values of q_e. The constants related to the non-linear form of Langmuir and Freundlich isotherms were determined by using same method.

Fig. 2 shows the experimental data fitted to non-linear form of these isotherms for Pb(II) ions adsorption by STWB. The isotherms constants related to Redlich–Peterson, Langmuir and Freundlich models determined from the plots shown Fig. 2 are listed in Tables 1–3, respectively. On the other hand, the linear plots of Langmuir and Freundlich models were constructed and the constants related to linear form were calculated and listed in Tables 2 and 3 to compare the values of them to those of non-linear models.

As seen from Fig. 2, the adsorption equilibrium data were fitted well to the Redlich–Peterson model which combines the features of Langmuir and Freundlich models. Correlation coefficients (R^2) for Redlich–Peterson model were determined in the range (0.964–0.996) for all temperatures studied. The constants A and B have an increasing trend up to 50 °C. As can be clearly seen from Table 1, the values of g tend to unity at the lower temperatures, which shows that the isotherms are approaching Langmuir form.

The constants q_{max} and K, together with correlation coefficients and isotherms equations, determined for the Langmuir isotherm from both non-linear and linear models are presented in Table 2. The results show that maximum adsorption capacity (q_{max}) calculated for linear and non-linear models increased as the temperature increased. There is no remarkable difference between the values of q_{max} calculated for two models. The values of q_{max} calculated from linear and non-linear models were found to be 55.56 and 52.33 mg/mg for the experiments carried out at 25 °C. The values of q_{max} for 60 °C were determined as 79.37 and 76.66 mg/g. Maximum adsorption capacity (q_{max}) is a most important parameter to compare the efficiency of adsorbents used. In a study carried out NaOH treated spent

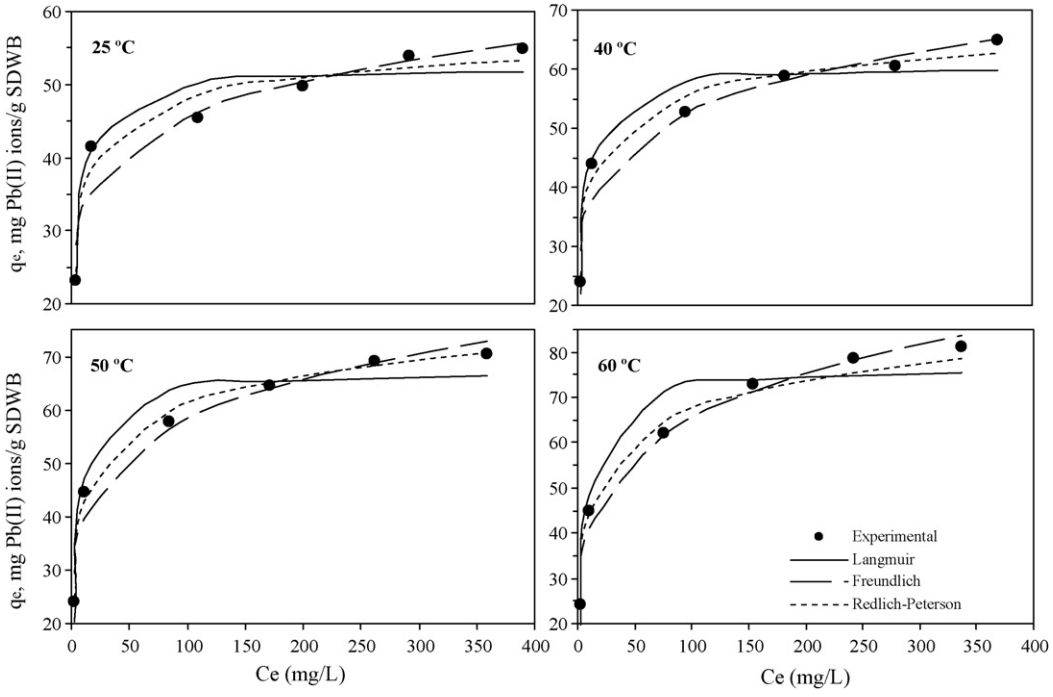

Fig. 2. Plots of non-linear isotherm models for Pb(II) adsorption on STWB (*conditions*: 0.1 g STWB, 50 mL Pb(II) solution at various concentration, final pH 6.0 ± 0.2, contact time: 120 min).

Table 1
Redlich–Peterson model equations and constants for Pb(II) ions adsorption on STWB

Temperature (°C)	Non-linear model				
	Model equation	Model constants			
		A (L/g)	B (L/mg)^g	g	R^2
25	$q_e = \frac{16.381C_e}{1+0.4354C_e^{0.940}}$	16.381	0.4354	0.940	0.964
40	$q_e = \frac{24.511C_e}{1+0.6190C_e^{0.921}}$	24.511	0.6190	0.921	0.984
50	$q_e = \frac{30.213C_e}{1+0.7841C_e^{0.896}}$	30.213	0.7841	0.896	0.996
60	$q_e = \frac{27.668C_e}{1+0.6889C_e^{0.883}}$	27.668	0.6889	0.883	0.988

Table 2
Langmuir model equations and constants for Pb(II) ions adsorption on STWB

Temperature (°C)	Non-linear model				Linear model			
	Model equation	Model constants			Model equation	Model constants		
		q_{max} (mg/g)	K (L/mg)	R^2		q_{max} (mg/g)	K (L/mg)	R^2
25	$q_e = 11.042C_e/(1+0.211C_e)$	52.33	0.211	0.941	$C_e/q_e = 0.2232 + 0.0180C_e$	55.56	0.0806	0.996
40	$q_e = 14.146C_e/(1+0.234C_e)$	60.53	0.234	0.949	$C_e/q_e = 0.1800 + 0.0154C_e$	64.94	0.0856	0.996
50	$q_e = 14.562C_e/(1+0.217C_e)$	67.11	0.217	0.946	$C_e/q_e = 0.1522 + 0.0140C_e$	71.43	0.0920	0.998
60	$q_e = 13.186C_e/(1+0.172C_e)$	76.66	0.172	0.945	$C_e/q_e = 0.12266 + 0.0126C_e$	79.37	0.0995	0.997

grain, the maximum adsorption capacity have been found to be 35.5 mg/g for Pb(II) ions adsorption [17]. The maximum Pb(II) uptake by sphagnum moss peat was 40.0 mg/g [33]. The values of q_{max} have been reported as 142.86–136.98 mg/g for Pb(II) ions adsorption at temperature range 20–40 °C in a study carried out by maize barn [6]. The maximum adsorption capacity was reported as 39.8 mg/g for tree fern [18]; 49.94 mg/g for grape stalks [11]; 21.96 mg/g for sawdust of *Pinus sylvestris* [34]. In a study performed by raw whet bran, maximum adsorption capacities have been obtained as 68.07, 80.65 and 86.96 mg/g at 20, 40 and 60 °C, respectively [19]. The values reported for raw wheat bran is slightly higher that of the STWB. This situation may be seen a paradox. It is probably that the adsorption of Pb(II) on wheat bran ions have been masked by precipitation, because it has not been reported the pH that the process was carried out. At this study, the removal percentages of Pb(II) ions were reported as 95.67, 97.74 and 95.55 for initial concentrations of 200, 400 and 1000 mg/L, respectively, using constant amount of wheat bran (10 g/L dosage). This is a clear evidence of precipitation of Pb(II) ions removed at the process used wheat bran as an adsorbent. Although direct comparison of maximum capacities of STWB with those of other adsorbents is difficult due to different experimental conditions applied in the studies cited, the STWB is a moderate adsorbent for the removal of Pb(II) ions from aqueous solution. Variation of the K values with temperature for non-linear model is not regular, but the values of them for linear model have increasing trend with a rise in temperature. As seen from Table 2, the values of correlation coefficients for linear model are very high compared to those of non-linear model, indicating that the equilibrium data obeyed well the linear Langmuir model. The increase in the values of q_{max} and K (for linear model) with temperature indicates that the Pb(II) ions are favourably adsorbed by STWB at higher temperatures, which shows that the adsorption of Pb(II) ions by STWB is endothermic.

The constants K_f and n for linear Freundlich model are obtained from the plots of $\ln q_e$ against $\ln C_e$ and presented in Table 3. The correlation coefficients determined for two models

Table 3
Freundlich model equations and constants for Pb(II) ions adsorption on STWB

Temperature (°C)	Non-linear model				Linear model			
	Model equation	Model constants			Model equation	Model constants		
		K_f	n	R^2		K_f	n	R^2
25	$q_e = 23.130C_e^{0.147}$	23.130	6.795	0.906	$\ln q_e = 3.054 + 0.1650 \ln C_e$	21.211	6.061	0.889
40	$q_e = 25.409C_e^{0.159}$	25.409	6.289	0.937	$\ln q_e = 3.142 + 0.1786 \ln C_e$	23.157	5.599	0.917
50	$q_e = 26.020C_e^{0.174}$	26.020	5.724	0.962	$\ln q_e = 3.159 + 0.11961 \ln C_e$	23.547	5.099	0.946
60	$q_e = 25.630C_e^{0.203}$	25.630	4.900	0.974	$\ln q_e = 3.145 + 0.2206 \ln C_e$	23.220	4.545	0.953

are relatively lower compared to those of other models, indicating that the data are not found in good agreement as that case of Langmuir and Redlich–Peterson models. But, the values of constant $K_{f,}$ which is a measure of adsorption capacity, are quite close to each other for same temperature. It observed that the values of constant n decreased with increasing temperature of solution for linear and non-linear form of Freundlich model. The values of n were obtained between 1 and 10, which represent a favorable adsorption [35]. It has been 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 [36].

3.3. Thermodynamic parameters

The determination of thermodynamics parameters has a great importance to evaluate spontaneity and heat change for the adsorption reactions. Equilibrium constant (K) obtained from linear Langmuir model plots can be used to determine the thermodynamic parameters.

The relationship between the adsorption equilibrium constant and temperature may be expressed by van't Hoff equation represented as follows:

$$\frac{\mathrm{d}(\ln K)}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{9}$$

Integrated form of this equation can be written as follows:

$$-\ln K = \frac{\Delta H}{R}\left(\frac{1}{T}\right) + C \tag{10}$$

If constant C is replaced with $-(\Delta S/R)$, Eq. (11) can be obtained.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R}\left(\frac{1}{T}\right) \tag{11}$$

If Eq. (11) combined with $\Delta G = -RT\ln K$ and rearrange the following equation is obtained.

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

where K is adsorption equilibrium constant, R the universal gas constant, 8.314 J/mol K and T is absolute temperature. ΔH, ΔS and ΔG are change in enthalpy, entropy and free energy, respectively.

The enthalpy and entropy change were determined by plotting $\ln K$ versus $1/T$. This plot was found to be linear (Fig. 3). ΔH and ΔS determined from the slope and the intercept of the plot are 4.89 kJ/mol and 97.2 J/mol K, respectively. The enthalpy and entropy changes have been determined as 11.55 kJ/mol and 60.00 J/mol K for a study carried out by raw wheat bran [19]. These results thermodynamically show that raw wheat bran has a similar behaviour with STWB. The positive value of ΔH confirms that the process is endothermic. This behaviour might be due to the increase in chemical interaction between adsorbate ions and surface functionalities of adsorbents or due to the increase of the intraparticle diffusion rate of adsorbate ions into the pores at higher temperature as diffusion is an endothermic process [37]. Endothermic adsorption processes have also been reported by some workers in their studies carried out with peat [14], activated phosphate [23] and activated carbon prepared from coconut shell [28]. Positive entropy change is possibly stemming from the changes take place in structure of adsorbent and dispersing of water molecules from Pb(II) ions surrounded by water molecules during adsorption process. By using Eq. (12), ΔG were calculated as −24.1, −25.5, −26.5 and −27.6 kJ/mol for 25, 40, 50 and 60 °C, respectively. The values of ΔG for raw wheat bran have been reported at range of 5.93–8.35 kJ/mol with a negative sign at temperature range studied (20–60 °C) [19]. The negative values of ΔG indicate the process to be feasible an adsorption to be spontaneous with high preference of Pb(II) ions for STWB. The decrease in the value of ΔG with increasing temperature indicated that the adsorption of Pb(II) ions on STWB became more favorable at higher temperature.

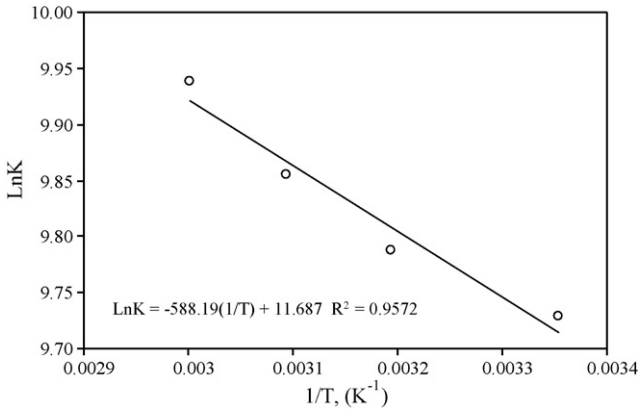

Fig. 3. Plot of free energy change (ΔG) vs. temperature.

3.4. Kinetic study

The determination of rate constant of adsorption process is necessary when designing an adsorption reactor. Various adsorption kinetic models have been used to describe the uptake of adsorbate depending upon the time. Lagergren model was known as first order kinetic model and based on the solid capacity [14,29]. This model is generally expressed as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{\mathrm{ad}}(q_{\mathrm{e}} - q_t) \tag{13}$$

This equation is rate expression for pseudo-first order reaction, where q_{e} (mg/g) is the amount of adsorbate adsorbed on the surface of the adsorbent at equilibrium, q_t (mg/g) the amount of adsorbate at any contact time. k_{ad} is the rate constant of adsorption reaction and its unit is depending upon the order of the reaction. Lagergren model may be written for nth order kinetic model as follows:

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

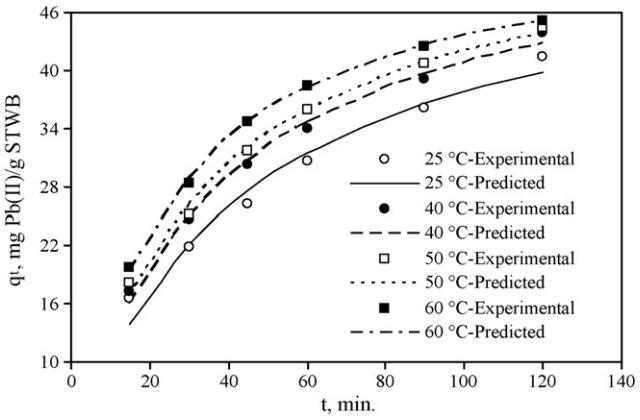

Fig. 4. Plot of pseudo *n*th order kinetic model for the adsorption of Pb(II) ions on STWB at various temperatures. (*conditions*: 50 mL 100 mg/L Pb(II) solution; 0.1 g STWB; final pH 6.0 ± 0.2).

If n equals 1, integrated form of Eq. (14) for the boundary conditions $t = 0$–t and $q_t = 0$–q_t, will give Eq. (15).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_{ad}}{2.303}t \tag{15}$$

If n equals 2, after integrating Eq. (14) for the same condition, Ho's pseudo-second order kinetic model equation will be obtained [38].

$$\frac{t}{q_t} = \frac{1}{k_{ad}q_e^2} + \frac{1}{q_e}t \tag{16}$$

I think that the direct calculation of rate constant and order of the adsorption reaction is a more appropriate method instead of assuming order of the reaction as 1 or 2. For that reason, to determine the rate constant and order of reaction from the kinetic data, Eq. (14) was integrated for pseudo-*n*th order and following non-linear equation was obtained.

$$q_t = q_e - \left[(n-1)k_{ad}t + q^{(1-n)}\right]^{1/1-n} \tag{17}$$

These constants were determined using non-linear regression programme of Statistica 6.0 software which uses Hooke-Jeeves and Quasi Newton estimation method based on the loss function $(q_{obs} - q_{pred})^2$ which minimizes the squares of difference between the observed and predicted values.

The variation of q_t determined from experimental data and non-linear kinetic model with respect to time t was given in Fig. 4 for temperatures of 25, 40, 50 and 60 °C. The shape of these plots depicted in this figure shows that the kinetic data are found in good agreement with *n*th order kinetic model. The *n*th order kinetic model parameters were determined and listed in Table 4. The order of adsorption reaction (n) was found to be between 1.711 and 1.929 at temperature range from 25 to 60 °C. The vales of n decreased slightly with rise in temperature. It is clearly that the values of n are close to 2 at the range of temperatures studied. If n is close to 2 means that the experimental data could fit appropriately the pseudo-second order equation and in this case it has been reported that chemisorption could be the rate-controlling step [39]. The values of k_{ad} determined from *n*th order kinetic models using non-linear regression analysis are found to be 5.82×10^{-4}, 7.98×10^{-4}, 11.13×10^{-4} and 21.81×10^{-4} $(min^{-1})(mg/g)^{1-n}$ at 25, 40, 50 and 60 °C, respectively. These results show that the adsorption Pb(II) ions by STWB is faster at higher temperatures. The experimental value of q_e and predicted value of q_e calculated from the *n*th kinetic model using non-linear regression programme are also given Table 4. As seen, there are certain difference between the experimental value of q_e and predicted value of q_e. . However, the correlation coefficients for the model were found to be higher than 0.99 except for 0.970 corresponding at 25 °C, indicating a highly significant relationship between the *n*th order kinetic model and experimental data.

The relation between rate constant and temperature may be described by the linear form of Arrhenius equation expressed in (Eq. (18)):

$$\ln k_{ad} = \ln k_o - \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{18}$$

where k_{ad} is rate constant of adsorption, k_o the temperature-independent factor has same unit with k_{ad}, E_a (J/mol) the activation energy, R (8.314 J/mol K) the ideal gas constant and T (K) is the solution temperature. To calculate activation energy (E_a) for adsorption process, $\ln k_{ad}$ were plotted versus $1/T$ and the following equation was found.

$$k_{ad} = 84.6 \exp\left(\frac{-3566.3}{T}\right) \tag{19}$$

From final equation, the activation energy for the process was found to be 29.65 kJ/mol. It has been reported that the activation energy for the adsorption of lead (II) by tree fern [39] and peat [40] were 87 and 29.8 kJ/mol, respectively. These findings were presented as evidence for chemical adsorption which is the rate-controlling step. The values of activation energy for the adsorption of Pb(II) ions on STWB suggested that the adsorption rate-controlling step is likely chemical adsorption.

Table 4
*n*th order kinetic model parameters for Pb(II) ions adsorption on STWB

Temperature (°C)	*n*th order kinetic model equation	q_e (mg/g)		n	$k_{ad}.10^4$ $(min^{-1})(mg/g)^{1-n}$	R^2
		Experimental	Predicted			
25	$q_t = 53.20 - (5.1 \times 10^{-4}t + 0.0249)^{-1.076}$	41.40	53.20	1.929	5.82	0.970
40	$q_t = 54.57 - (7.03 \times 10^{-4}t + 0.0295)^{-1.135}$	43.91	54.57	1.881	7.98	0.991
50	$q_t = 54.44 - (9.06 \times 10^{-4}t + 0.0385)^{-1.228}$	44.50	54.44	1.814	11.13	0.994
60	$q_t = 52.29 - (1.55 \times 10^{-3}t + 0.0599)^{-1.406}$	45.20	52.29	1.711	21.81	0.999

4. Conclusions

The results of this study show that sulphuric acid-treated wheat bran (STWB) may be used as an effective adsorbent to remove Pb(II) ions from aqueous solution. The removal yield increased with increasing contact time and reached the equilibrium state within 2 h. The adsorption of Pb(II) ions dependent on the pH of the solution and maximum removal at 6.0 ± 0.2 was found to be 82.8% at 25 °C. At same conditions, the removal percentage of Pb(II) ion by raw wheat bran was found to be 42.1%. The equilibrium data fitted to the Langmuir, Freundlich and Redlich–Peterson model. Non-linear Redlich–Peterson model has higher correlation coefficients than those of non-linear Langmuir and Freundlich models. However, the correlation coefficients determined for linear Langmuir models were higher than those of others. The values of q_{max} obtained from linear Langmuir model increased from 55.56 to 79.37 mg/g, when the solution temperature increased from 25 to 60 °C. The enthalpy (ΔH) and entropy change (ΔS) were calculated as 4.89 kJ/mol and 97.2 J/mol K. Positive values of enthalpy change indicate the endothermic nature of the adsorption process. Free energy change (ΔG) with negative sign reflects the feasibility and spontaneous nature of the process. The kinetic analysis showed that the adsorption of Pb(II) ions onto STWB could be described well with the *n*th order kinetic model. The rate constants have an increasing trend with temperature, which indicated that the adsorption Pb(II) ions by STWB was faster at higher temperatures.

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