Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons

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Present study explored the feasibility of using waste rice-straw based carbons as adsorbent for the removal of strontium under different experimental conditions. The batch sorption is studied with respect to solute concentration (2.8 - 110 mg/L), contact time, adsorbent dose (2.5 - 20 g/L) and solution temperature (25 - 55 $^{\circ}$C). The Langmuir and Dubinin-Radushkevich adsorption models were applied to experimental equilibrium data and isotherm constants were calculated using linear regression analysis. A comparison of kinetic models applied to the adsorption of strontium on rice-straw carbon was evaluated for the pseudo-second-order, Elovich, intraparticle diffusion and Bangham's kinetics models. The experimental data fitted very well the pseudosecond-order kinetic model and also followed by intra-particle diffusion model, whereas diffusion is not only the rate-controlling step. The results show that the sorption capacity increases with an increase in solution temperature from 25 to 55 $^{\circ}$C. The thermodynamics parameters were evaluated. The positive value of ΔH (40.93 kJ) indicated that the adsorption of strontium onto RS_1 carbon was endothermic, which result was supported by the increasing adsorption of strontium with temperature. The positive value of ΔS (121.8 kJ/mol) reflects good affinity of strontium ions towards the rice-straw based carbons. The results have established good potentiality for the carbons particles to be used as a sorbent for the removal of strontium from wastewater.

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1. Introduction : The annual harvest and processing of various agriculture crops grown in Egypt yields considerable quantities of agricultural by-products, about 25 million tons per year of agro-residues are estimated, of which 12 million tons are used in energy production or for industrial purposes. Another 3 million tons are used to produce biogas. The remaining is burned directly. The waste products, which are the main contributors to biomass burning, are wheat residue and rice straw. Rice straw is a lignocellulosic agricultural by-product containing cellulose (37.4 %), hemi-cellulose (44.9 %), lignin (4.9 %) and silicon ash (13.1 %) [11]. The disposal of rice straw by open-field burning frequently causes serious air pollution, hence new economical technologies for rice straw disposal and utilization must be developed. In recent years, attention has been focused on the utilization of native agricultural by-products as sorbent [3, 8, 20]. Generally, the sorption capacity of native agricultural by-products is low. In order to improve the sorption capacity of these biomaterials, the agricultural by-products were converted to activated carbon.

The manufacturing processes of activated carbons in laboratory scale may be categorized into two groups. That is, one includes the synchronous process of carbonization and activation (denoted the one-stage process), the other is the asynchronous process in which a separate carbonization process is included prior to the activation process (denoted the two-stage process) [18]. If the precursor is heat treated by one of the above-mentioned two processes, the resultant activated carbons should naturally have different burn-off ratios and thus different pore characteristics and adsorption capacities since the two processes have definite differences in thermal history. One-step procedure appears to be preferable because of lower activation temperature used, thereby reducing production costs in term of energy and time saving. This process results in activated carbon with high adsorption capacity [17].

On the other hand, the removal of radioactive strontium from nuclear waste solutions is important from the point of view of their biotoxicity and therefore has been of interest [19]. Because of chemical similarity between strontium and calcium, strontium is easily incorporated into bone and continues to irradiate localized tissues with the eventual development of bone sarcoma and leukemia [5]. Radioactive solid waste arises during the maintenance and the repair of the nuclear power plants or the nuclear fuel cycle facilities. The solid waste can be recycle and the amounts of disposal waste can be reduced significantly by application of the proper decontamination technology. Therefore, it is necessary to treat the secondary waste to increase the decontamination efficiency. One of the efficient methods to treat the secondary waste is the sorption.

The objectives of this work were to use of rice straw as a raw material for the production of an activated carbon using one-stage steam pyroysis and to study the feasibility of using this carbon as an adsorbent for strontium ions removal from wastewater. In doing so, the adsorption of strontium on this waste material from aqueous solutions was evaluated in batch experiments. The adsorption isotherms, kinetics and temperature effect were studied.

2. Experimental :
2.1. Materials and methods :
2.1.1. Adsorbent : Our previous study [24] explored the feasibility of utilizing waste rice straw as adsorbent for uranium and thorium removal from aqueous solution, then, this rice straw based carbon was used for adsorption of strontium ions in this work. For the preparation of rice straw carbon, 0.5 Kg dried Rice Straw is feed into fluidized bed reactor, described elsewhere [24], at heating rate $50^oC/10$ min in the presence of N_2 flow (300 ml/min). The steam entered the reactor at a rate of 5 ml/min when the furnace reached 350 ^oC and the heating continued up to final temperature of 550, 650, 750 ^oC, holds at this temperature for one hour. The furnace is switched off. The carbon was left to cool down and washed with distilled water, dried at 120 °C and stored in stoppered bottles. The samples were taken the abbreviations, RS_1, RS_2, and RS_3 for carbons activated at 550, 650, and 750 ^oC respectively.

2.1.2. Absorbate : Stock solutions were prepared by dissolving accurately weighed samples of strontium chloride in distilled water to give a concentration of 1000 mg/L and diluted with distilled water when necessary.

2.2. Kinetic studies : 20 mg of the adsorbent in 25 ml reagent bottles containing 10 ml of strontium solution (30 ppm) were mixed and placed in the shaker at constant temperature for different time intervals. The adsorbent was finally removed by filtration, strontium concentration was determined. The contact time required for complete metal adsorption was determined and utilized in the remaining tests.

2.3. Equilibrium studies : Adsorption equilibrium studies were conducted at initial strontium solution pH of 6 - 7. Equilibrium data were obtained by adding 0.005 – 0.1 g of rice straw carbon into a series of conical flasks each filled with 10 mL of strontium solution (5 ppm). The conical flasks then covered with aluminum foil and were then placed in a thermostatic shaker for 4 h at 25 ^oC. The removal efficiency (E %) of strontium on rice straw carbon, the sorption capacity, (q) and distribution ratio (K_d) were calculated from equations (1 –3) :
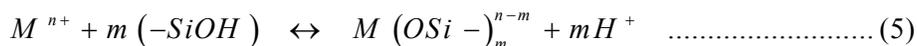
$$E(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad\quad\quad ....(1)$$

$$q = \frac{V(C_i - C_e)}{m} \quad\quad\quad ....(2)$$

$$k_d = \frac{amount\ of\ strontium\ in\ adsorbent}{amount\ of\ stronium\ in\ solution} \times \frac{V}{m}\ (L/g) \quad ....(3)$$

where C_i and C_f are the initial and final concentrations of strontium (mg/L) in aqueous solution, respectively, V is the volume of the solution (ml) and m represents the weight of the adsorbent (mg).

3. Results and Discussion : Preliminary experiments show that rice straw activated at 550 ^{o}C (RS$_1$) gives the highest adsorption for strontium compared to the other carbon adsorbents (RS$_2$ and RS$_3$). Therefore, RS$_1$ carbon was selected for further detailed experimental investigations. The aim was to find out the effect of various parameters on its affinity towards the uptake of strontium using RS$_1$ carbon.

3.1. Effect of pH : It is known that pH is important factor for the adsorption of metal ions on the adsorbents. The dependence of adsorption of strontium ions on the RS$_1$ carbon was also analyzed by plotting adsorption uptake of Sr (II) ions as a functional pH at a constant initial concentration (18 mg/L) in Figure (1). It is clear that a marked influence with a gradual rise in the uptake with increase in pH from 2 to 10. According to pH results, we can assume that Sr (II) ion in solution can able to bind chemically with carboxyl groups in the carbon. This means that an ion-exchange reaction takes place in the adsorption of Sr (II) ion. Rice straw based carbon contain silica (SiO$_2$) and the hydrolysis of silicon dioxide produces hydrous oxide surface group -SiOH i.e., silanol group. The ion-exchange reaction is accomplished through the substitution of protons of the surface carboxyl and silanol group by strontium ion, according to the following reactions [13] :

$$M^{n+} + m\left(-COOH\right) \quad \leftrightarrow \quad M\left(OOC-\right)_m^{n-m} + mH^+ \quad \text{......................} (4)$$

$$M^{n+} + m\left(-SiOH\right) \quad \leftrightarrow \quad M\left(OSi-\right)_m^{n-m} + mH^+ \quad \text{..........................} (5)$$

where M^{n+}= metal ion with n+ charge, -COOH = carboxyl group, -SiOH = silanol group, and mH$^+$ = number of protons released.

In such a system, at low pH, because of the high concentration of H$^+$, equation (4 and 5) lies to the left. The ion exchange sites are mainly protonated and are less available for ion exchange. Equations (4 and 5) proceed further to the right and metal ion removal is increased by increased pH. Within this pH range, the ion exchange process is the major mechanism for removal of metal ion from solution.

In the subsequent studies, experiments were performed in the solution pH value of 6 to avoid any possible hydroxide precipitation.
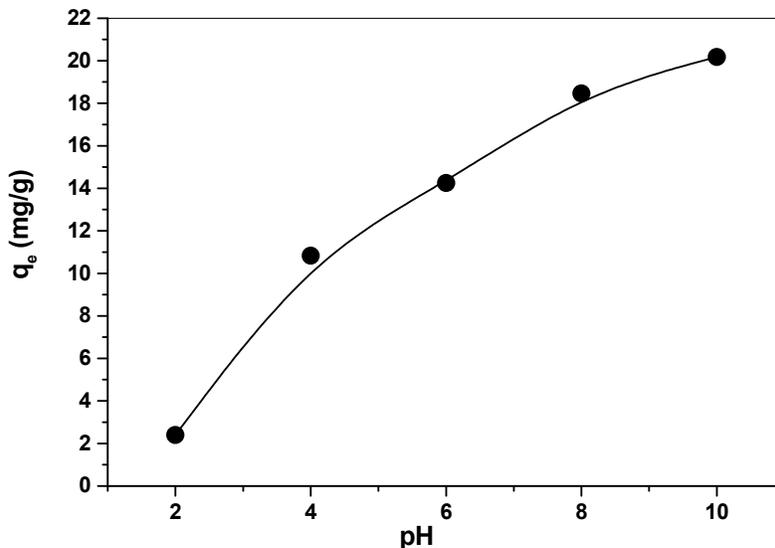

Figure (1) : Effect of strontium adsorption onto RS1 carbon.

3.2. Effect of contact time and temperature : The influence of contact time on the amount of strontium adsorbed by RS$_1$ was investigated at various temperatures as shown in Figure (2). It is seen that the amount of adsorption increased with increasing the contact time. Maximum adsorption was observed after 1 h, beyond which there was almost no further increase in the adsorption. This was therefore fixed as the equilibrium contact time. The equilibrium adsorption capacity of strontium onto RS$_1$ was found to increase with increasing temperature, increasing from 12.7 mg/g at 25 ◦C and 14.6 mg/g at 35 ◦C to 30 mg/g at 55 ^{o}C indicating that the strontium ion adsorption on the adsorbent was favored at higher temperatures. The sorption of strontium is endothermic, thus the extent of adsorption increased with increasing temperature. The sorption of strontium by

rice straw activated carbon involves not only physical but also chemical sorption. At high temperature, ions are readily dehydrated, and therefore their adsorption becomes more favorable.
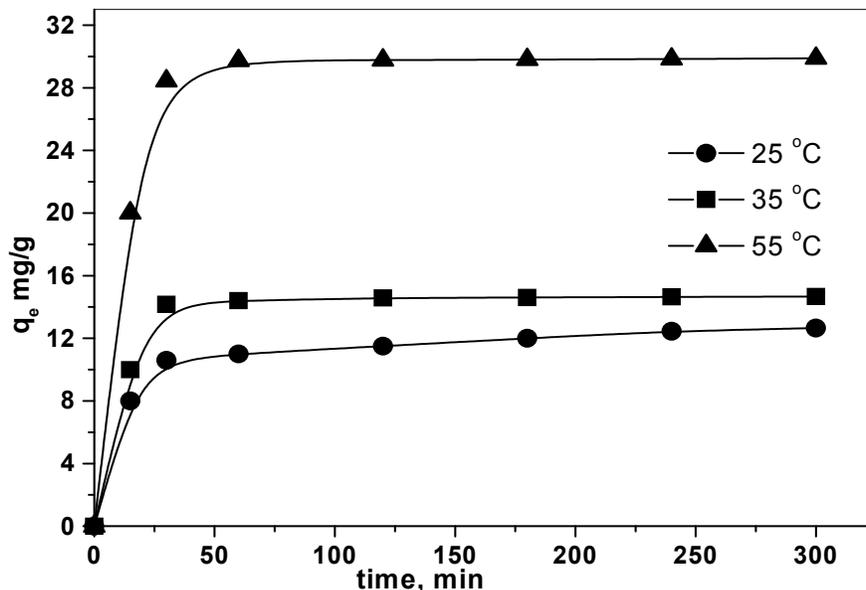

Figure (2) : Effect of contact time at several solution temperatures on sorption kinetics b onto RS_1 carbon.

3.4. Adsorption isotherms : The adsorption data were analyzed to see whether the isotherm obeyed the Langmuir [15] and Dubinin-Radushkevich (D-R) [7] isotherm models equations.

$$\text{Langmuir equation}: \quad \frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max}k_L}\right)\frac{1}{C_e} \quad \text{.......................................(6)}$$

$$\text{D – R equation}: \quad \ln q_e = \ln q_m - \beta\varepsilon^2 \quad \text{.......................................(7)}$$

where q_{max}, the monolayer capacity of the adsorbent (mg/g); K_L, the Langmuir constant (L/mg) and related to the free energy of adsorption; q_m, the theoretical saturation capacity (mg/g); and ε, the Polanyi potential, which is equal to RT ln(1 + (1/C_e)), where R (J/mol K) is the gas constant and T (K) is the absolute temperature; β, a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/kJ^2). q_{max} and K_L, of Langmuir equation can be determined from the linear plot of 1/C_e versus 1/ q_e. q_m and β of D-R equation can be determined by plotting ln q_e versus ε^2 (figure not given).

The Langmuir, and D-R parameters for the adsorption of strontium adsorption onto RS_1 carbon being listed in Table (1). The fit of the data for strontium adsorption onto RS_1 carbon suggests that the D-R model gave better fittings than of Langmuir models, as is obvious from a comparison of the r^2 in Table (1).

The constant β gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [6] :

$$E = \frac{1}{(2\beta)^{1/2}} \quad \text{.......................................(8)}$$

The numerical value of adsorption of the mean free energy is 9.7 kJ/mol (Table 1) corresponds to ion exchange process [10] that confirms results from pH effect in section (3.1).

Table (1) : Isotherm constants for the adsorption of for strontium adsorption onto RS_1 carbon.

Langmuir	
q_{max} (mg/g)	2.3
K_L (L/mg)	26.2
R^2	0.93
D-R	
q_m (mg/g)	$7.3 \ 10^{-2}$
β (mol^2/kJ^2)	5.36×10^{-3}
R^2	0.97
E (kJ/mol)	9.7

3.5. Kinetic models : The studies of adsorption equilibrium are important in determining the effectiveness of adsorption; however, it is also necessary to identify the types of adsorption mechanism in a given system. In this study we used four different models to predict the adsorption kinetic of strontium on RS_1 carbon (pseudo-second-order, Elovich, intra-particle diffusion and Bangham) models.

3.5.1. Pseudo-second-order model : Based on equilibrium adsorption, the pseudo-second-order kinetic equation [12] is expressed as :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(9)$$

where K_2 is the rate constant of pseudo-second-order adsorption (g/mg min) and q_t (mg/g) the amount of adsorbate retained at time (t).

The initial adsorption rate, h, (mg/g min) is expressed as :

$$h = k_2 q_e^2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(10)$$

Both constants K_2 and h can be calculated from the intercept and slope of the line obtained by plotting t/qt versus t. The values of model parameters (K_2, h and q_e) for different temperatures, under the initial concentration of 30 mg/L, are given in Table (2), It can be seen that the kinetics of strontium ion adsorption onto RS_1 carbon follow this model with correlation coefficients higher than 0.999 and the equilibrium adsorption capacity, q_e, increases as adsorption temperature increased from 25°C to 55 °C. For example, the values of q_e increased from 13 mg/g at 25 °C to 30 mg/g at 55 °C. Also, from Table (2), it was noticed that the initial adsorption rate, h, increases with increasing temperature. These results imply that chemisorption mechanism may play an important role for the adsorption of strontium on RS_1 carbon.

3.5.2. Elovich model : Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate–adsorbent [21]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [26]. The linear form of this equation [21] is given by :

$$q_t = \frac{\ln a_e b_e}{b_e} + \frac{1}{b_e} \ln t \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(11)$$

where a_e is the initial adsorption rate (mg/g min), and the parameter b_e is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

The Elovich coefficients could be computed from the plots q_t versus ln t. The initial adsorption rate, a_e, and the desorption constant, b_e, were calculated from the intercept and slope of the straight-line plots of q_t against lnt . Table (2) lists the kinetic constants obtained from the Elovich equation. It will be seen that applicability of the simple Elovich equation for the present kinetic data indicates that the Elovich equation was able to describe properly the kinetics of strontium adsorption on RS_1 carbon. The value of a_e and b_e varied as a function of the solution temperature. Thus, on increasing the solution temperature from 25 to 55 °C, the value of b_e decreased

from 0.8 to 0.4 g/mg due to the less available surface for strontium ions. On the other hand, an increase in the solution temperature from 25 to 55 ^{o}C leads to an increase in the value of a_e from 4.4 to 7.7 mg/g min. This means that adsorption increased while desorption decreased during increasing solution temperature. However, the experimental data did not give a good correlation for these results at high solution temperature.

Table (2) : Comparison of the pseudo second-order, Elovich, Intra-particle diffusion and Bangham's adsorption rate constants and the calculated and experimental q_e values at 25 ^{o}C, 35 ^{o}C and 55 ^{o}C.

Model	Parameter	Temperature		
		25°C	35°C	55°C
	$q_{e,exp}$ (mg/g)	12.7	14.7	29.9
Second-order model	K_2 (g/mg min)	0.007	0.019	0.009
	q_e(mg/g)	13.02	14.87	30,3
	h (mg/g min)	1.19	4,3	8.7
	R^2	0.9997	0.9998	0,9998
Elovich model	a_e(mg/g min)	4.4	7.5	7.7
	b_e (g/mg)	0.8	0.86	0.4
	R^2	0.95	0.8	0.8
Intra-particle diffusion model	K_i (mg/g min1/2)	9.72	14.05	28.51
	C	0.167	0.039	0.091
	R^2	0.99	0.93	0.74
	D_i (cm^2/s)	$0.9 * 10^{-11}$	$1 * 10^{-11}$	$1.3 *10^{-11}$
Bangham's model	K_b (mL/g/L)	0.87	1.58	3.9
	α	0.09	0.02	0.03
	r^2	0.99	0.97	0.82

3.5.3. Intra-particle diffusion model : The pseudo-second-order and Elovich kinetic models could not identify the diffusion mechanism and the kinetic results were then analyzed by using the intra-particle diffusion model. In the model developed by Weber and Morris [23], McKay and Poots [16], the initial rate of intra-particle diffusion is calculated by linearization of equation (12) :

$$q_t = k_i t^{½} + C \qquad\qquad ....(12)$$

where C is the intercept and K_i is the intra-particle diffusion rate constant (mg/g min$^{1/2}$).

According to this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step [1]. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and this further show that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously.

The intra-particle diffusion, K_i, values were obtained from the slope of the straight-line portions of plot of qt versus $t^{1/2}$ for various solutions temperature. The correlation coefficients (R^2) for the intraparticle diffusion model are between 0.99 at 25 ^{o}C and decreases by increasing temperature (Table 2). It was observed that intra-particle rate constant values (K_i) increased with solution temperature. Increasing the temperature promoted the pore diffusion in sorbent particles and resulted in an enhancement in the intra-particle diffusion rate. It is likely that a large number of ions diffuse into the pore before being adsorbed. It was observed that the straight lines did not pass through the origin and this further indicates that the intra-particle diffusion is not the only rate-controlling step.

Also, the diffusion coefficients for the intra-particle transport of strontium ion within the pores of carbon particles have been calculated by employing equation (13) [3].

$$D_i = \frac{0.03 \times r^2}{t_{1/2}} \qquad \text{...(13)}$$

where D_i is the diffusion coefficients with the unit cm^2/s; $t_{1/2}$ is the time (s) for half-adsorption of strontium species and r is the average radius of the adsorbent particle in cm. The value of r (average radius) was calculated as 5×10^{-4} cm. In these calculations, it has been assumed that the solid phase consists of spherical particles.

The diffusion coefficients varied from 0.9×10^{-11} to 1.3×10^{-11} cm^2/s with an increase of solution temperature from 25 to 55 °C. At higher temperatures the attraction between the functional groups RS_1 carbon and strontium species gets stronger. The values of the internal diffusion coefficient, D_i, shown in Table (2) fell well within the magnitudes reported in literature [4], specifically for chemisorption system (10^{-5} to 10^{-13} cm^2/s), Kinetic data can further be used to check whether pore diffusion is the only rate-controlling step or not in the adsorption system by using Bangham's equation.

3.5.4. Bangham's model : Bangham's model [2] equation is generally expressed as

$$\log \log \left[\frac{C_i}{C_i - C_s q_t} \right] = \log \left[\frac{K_b C_s}{2.303 V} \right] + \alpha \log t \qquad \text{..................................(14)}$$

where C_s the weight of adsorbent used per liter of solution (g/L), α (<1) and k_b are constants. $\log[C_i/C_i - C_s q_t]$ was plotted against log t. The strontium adsorption fits the Bangham's model. α and k_b constants were calculated from the intercept and slope of the straight line plots of $\log[C_i/C_i - C_s q_t]$ against log t. If the experimental data is represented by this equation then the adsorption kinetics are limited by the pore diffusion [22].

Table (2) lists the kinetic constants obtained from the Bangham's equation. It will be seen that the value of α and k_b varied as a function of the solution temperature. Thus, on increasing the temperature, the value of α decreased and the value of k_b increased. The experimental data did not give a good correlation 55 °C ($r^2 = 0.82$). In addition, it was found that the correlation coefficients for the Elovich model are higher than those obtained for Bangham's model. This result still confirmed that the pore diffusion is not the only rate-controlling step.

3.6. Thermodynamic parameters : In any adsorption process, both energy and entropy considerations must be taken into account in order to determine what process will occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. Diffusion coefficient of strontium adsorption is expressed as a function of temperature by the following Arrhenius type relation :

$$D_i = D_o e^{-E_a/RT} \qquad \text{..(15)}$$

where E_a is the Arrhenius activation energy of adsorption; and the other terms have their usual meaning. A plot of ln D_i vs. 1/T was found to be linear (Figure 3). The E_a value calculated from the slope of the plot is equal to 10.1 kJ mol^{-1}. The relatively low activation energy suggested that Sr adsorption is a diffusion-controlled process. This result was also consistent with the value of the mean free energy E (9.7 kJ mol−1) from D-R isotherm model.

The other thermodynamic parameters, change in the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), were determined by using following equations [9] :

$$\Delta G^o = -RT \ln k_d \qquad \text{..(16)}$$

$$\ln k_d = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad \text{..(17)}$$

The values of ΔH (40.93 kJ) and ΔS (121.8 kJ/mol) were determined from the slope and intercept of the plot of ln K_d versus 1/T (Figure 4). The ΔH and ΔS values are positive. The positive values ΔH indicate the presence of an energy barrier in the adsorption and endothermic process [9]. The positive value of entropy change (ΔS) reflects good affinity of strontium ions towards the sorbent and the increasing randomness at the solid-solution interface during the adsorption process [25].

The ΔG value decreases from 4.3 to 0.8 kJ/mol when the temperature increases from 25 to 55 ^{o}C (Table 3), suggesting the more adsorbable of strontium species with increasing temperature.

Table (3) : Thermodynamic parameters.

T(^{o}C)	ΔH^o (kJ/mol)	ΔS^o (J/mol k)	ΔG^o (KJ/mol)
25°C	40.93	121.8	4.3
35°C	40.93	121.8	3.9
55°C	40.93	121.8	0.8
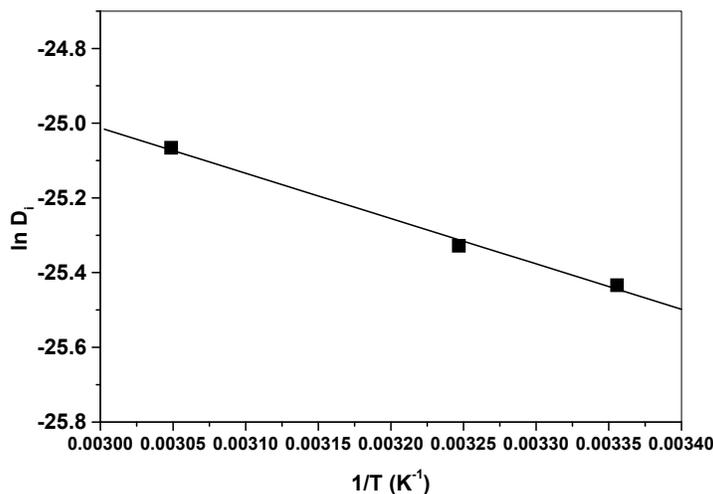
Figure (3) : Arrhenius plots for the adsorption of strontium onto RS$_1$ carbon at various temperatures.
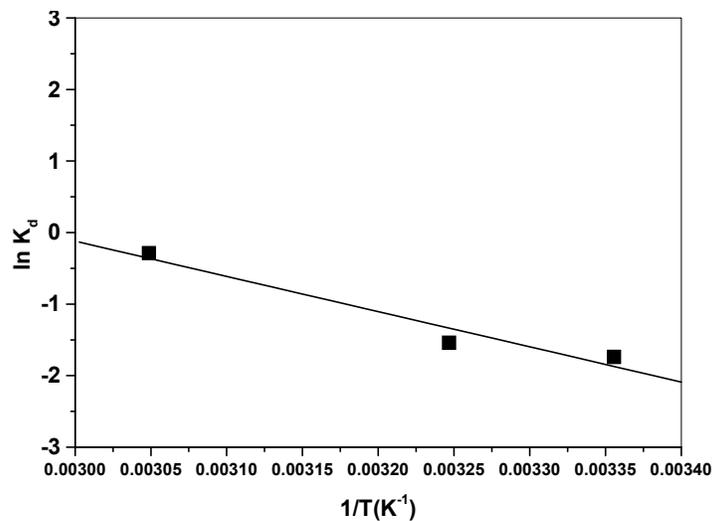
Figure (4) : Van't Hoff plot for the adsorption of strontium onto RS$_1$ carbon at various temperatures.

4. Conclusions : This study investigated the equilibrium and the dynamics of the adsorption of strontium onto activated carbon prepared by one stage steam pyrolysis of rice straw. The adsorption was found to be strongly dependent on pH, contact time and temperature. The adsorption of strontium was endothermic in nature with the metal removal capacity increasing with increasing temperature. The Langmuir and D-R adsorption models were used for the mathematical description of the adsorption equilibrium of strontium ions by rice straw carbon. The experimental data fitted well to the D-R adsorption isotherm. The kinetics of adsorption of Sr (II) on rice straw carbon was studied by using five kinetic models. The adsorption proceeds according to the pseudo-second-order

model which provides the best correlation of the data in all cases and the experimental qe(exp) values agree with the calculated ones. Also, it was observed that the intra-particle diffusion was not the only rate-controlling step. According to Elovich and Bangham model, the results show that the rate could be enhanced by increasing the adsorption temperature. Positive **ΔH** and **ΔS** values indicated that the adsorption of strontium rice straw carbon was endothermic, strontium ions has good affinity towards the sorbent and the increasing randomness at the solid-solution interface during the adsorption process.

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