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**KINETICS AND THERMODYNAMIC STUDIES ON REMOVAL OF CADMIUM METAL ION FROM AQUEOUS SOLUTION USING RICE STRAW**

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**Abstract**

The removal of Cd(II) from aqueous solution by batch adsorption technique using rice straw (SIII) and its ash (R400), in absence and presence of 0.005M hydrochloric acid were used to determine the adsorption efficiency. Kinetic studies were performed to understand the mechanistic steps of the adsorption process and the rate kinetics for the adsorption of Cd(II). The kinetic data supports pseudo-second order model and intra-particle model but shows very poor fit for pseudo-first order model. Thermodynamic parameters including the Gibbs free energy, enthalpy, and entropy indicated that the adsorption of Cd(II) ions was feasible, spontaneous in absence of HCl and exothermic in all media under studying, at temperature range of 25–45 °C.

**Keywords:** Cadmium (II); Rice Straw; Removal

**Introduction**

Heavy metals in natural or industrial wastewaters is a subject of great interest in environmental science which is one of the most serious worldwide environmental problem [1,2].

Cadmium like other heavy metals can be introduced into surface waters in amounts significant to human health by industrial effluents [3]. Cd, which is very toxic, can cause serious damage to the kidneys and bones. The major sources of cadmium are industrial water such as metal plating, cadmium-nickel batteries, phosphate fertiliser, mining, pigments, stabilisers and alloys [4].

The methods used to remove heavy metal ions are chemical precipitation, adsorption, ion-exchange, reverse osmosis, electrodialysis, electrochemical reduction, etc. Adsorption process is the most frequently applied method in industries [5].

Adsorption on activated carbon [6–11] is the most widely used method for removal of heavy metal ions because of the simplicity of the procedure in comparison to other methods. However, the use of activated carbon is not

economical for small scale industries. Recently, the adsorbents based on natural products and their derivatives have gained particular attention, e.g. sawdust [12–14], sugar beet pulp [15, 16], rice husk [17–20], treated rice husk [21], orange waste [22], bamboo charcoal [23], and treated orange waste [24].

Rice straw is an agricultural waste, obtained from the rice mills. It accounts for about one-fifth of the annual gross rice production of 545 million metric tons, of the world [25]. Rice straw is mostly used as a fuel in the boiler furnaces of various industries to produce steam. Since rice straw ash is available in plenty and it has very high potential as an adsorbent, the present study has been undertaken to report in detail the adsorption characteristics of rice straw and its ash for Cd(II) ions from aqueous solutions in absence and presence of 0.005 M hydrochloric acid solution.

## Materials and methods

### Instrumentation

AAS Vario 6 Analytik Jena atomic adsorption spectrometer operating with an air acetylene flame was used to analyze the concentration of heavy metals. Five standard solutions with concentrations of cadmium metal ions in the linear range of the instrument were used to construct each calibration curve. During analysis of the samples for cadmium metals concentration, those samples in which the concentration of cadmium metals is observed beyond the linear range of the references were diluted to appropriate concentrations. All measurements were repeated three times and those results in which the standard deviations were found greater than 0.1 mg/l were not accepted.

The pH of the solution was measured with a microprocessor pH Meter (PH 211) using HANNA electrode (HI1230) calibrated with standard buffer solutions of pH values: 4, 7, and 10.

### Adsorbate solution

Synthetic stock solution of cadmium metal ions was prepared by dissolving required quantity of Analar grade salts in the distilled water. The salts used are cadmium sulfate for the preparation of stock solution of Cd(II). The stock solution was further diluted with distilled water to desired concentration for obtaining the test solutions.

To prepare the rice straws, they were initially ground and homogenized using a food blender with steel blades for 10 min. Particle sizes  $\leq$  212 mesh (SIII), were obtained by passing the milled material through a steel sieve. Also SIII of rice straws was burn-off at 400°C (R400).

### **Batch mode adsorption studies**

Batch process was employed for adsorption studies. A 0.5 g adsorbent was placed in a polypropylene bottle having 100 ml of Cd(II) solution. The mixture was then filtered at predetermined time interval and the final concentration of metal ions was determined in the filtrate by Atomic Absorption Spectrophotometer. Amount of Cd(II) adsorbed was then calculated by subtracting final concentration from initial concentration. Adsorption studies were carried out by varying the adsorbate concentration ( $10 \text{ mg l}^{-1}$ ), the agitation time (3–180 min), and adsorbent amount (0.5 g).

The amount of cadmium adsorbed,  $q_e$  ( $\text{mg g}^{-1}$ ) was computed by using the following expression:

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

where  $C_0$  and  $C_e$  are cadmium ion concentrations ( $\text{mg L}^{-1}$ ) before and after adsorption,  $V$  is the volume of adsorbate (L) and  $m$  is the weight of the adsorbent (g). The percent removal of cadmium ion is calculated by the following equation:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

### **Effect of temperature**

Equilibrium adsorption of Cd(II) ions was performed at five different temperatures such as 25, 30, 35, 40, 45°C in absence and presence of 0.005M hydrochloric acid solution. Dose of 0.5 g of SIII, or R400 of rice was firstly weighed accurately and introduced directly into 250 ml polypropylene bottle. Then, 100ml of aqueous solutions containing metal ions with 10 mg/l concentration were added to each bottle and shacked till 3 h to attain the equilibrium. The concentration of the residual aqueous phase was determined using an atomic absorption spectrophotometer.

### **Kinetic studies**

Batch kinetic experiments were carried out in absence and presence of 0.005M hydrochloric acid (pH ~2.3) and adsorbent dose of 10 mg/l at a temperature of 25 °C. After shaking, the solution samples were withdrawn at suitable time intervals.

Batch equilibrium experiments were conducted using 250 ml polypropylene bottles at a total sample volume of 100 ml for each adsorption run. The samples were shaking to reach equilibrium. At the end of the reaction time (15 min), a known volume of the solution was removed for Cd(II) analysis. The residual metal ion concentrations were determined using atomic absorption spectrophotometer.

## **Results and discussion**

### **Efficiency of adsorption**

#### **Effect of acid concentration**

Table 1, shows the effect of acid concentration on the adsorption behavior of the cadmium metal ion onto SIII and R400 as observed in batch adsorption tests. The removal efficiency of cadmium metal ions onto SIII increased when the initial acid concentration (pH ~ 2.3) was decreased. It is assumed from the results that the governing mechanism during the removal is probably due to the ion exchange.

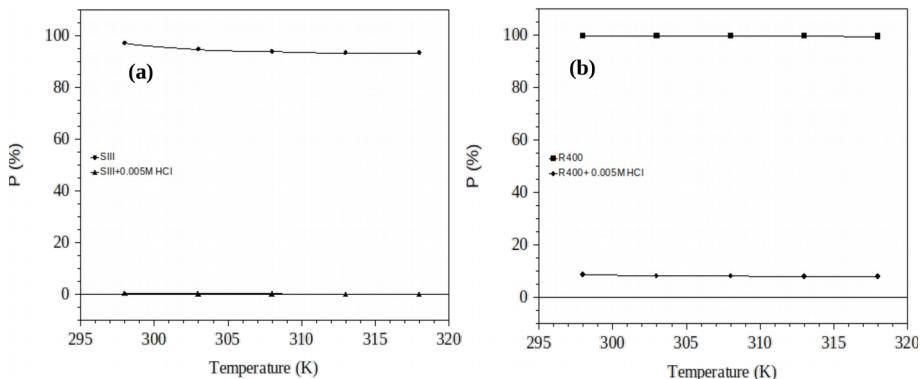
Also, Table 1 shows the effect of acid concentration on cadmium metal ion removal efficiencies of R400. These studies were conducted at a constant initial metal ions concentration of 10 mg/l. The adsorption efficiency decreases with add 0.005M of hydrochloric acid concentration.

At low pH (0.005M acid concentration), decreasing in efficiency may be due to high positive charge density on the surface sites, electrostatic repulsion between metal ion and H<sup>+</sup> ion will be high during uptake of metal ions resulting in lower removal efficiency. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density of proton on the sorption sites thus resulting in an enhancement of metal adsorption.

#### **Effect of temperature**

The effect of temperature on the adsorption of cadmium with initial concentration 10 mg/L was studied using adsorbent dose (0.5 g/100 mL) of SIII or R400 in absence and presence of 0.005M hydrochloric acid solution. Fig. 1. shows

the representative plots of adsorption efficiency versus temperature for Cd(II) at different temperatures ranging from 25 to 45 °C and agitation time three hours.



**Fig. (1): Effect of temperature on efficiency of cadmium ions adsorption on (a) SIII, and (b) R400, in absence and presence of 0.005M HCl.**

An increase in the temperature from 25 to 45 °C leads to slightly decrease in the adsorption capacity of SIII and R400 in absence and presence of hydrochloric acid solution. This may indicate that adsorption of cadmium (II) ions onto SIII+0.005M and R400+0.005HCl are exothermic.

**Table 1. Efficiency of cadmium ions adsorption on SIII, R400 in absence and presence of 0.005 M HCl at 25°C.**

| Adsorbent and adsorption media | Adsorption efficiency |
|--------------------------------|-----------------------|
| SIII                           | 97.1                  |
| SIII+ 0.005M HCl               | 0.5                   |
| R400                           | 99.6                  |
| R400+ 0.005M HCl               | 8.8                   |

### Adsorption kinetics study

To describe the kinetic process, kinetic data were analyzed based on Lagergren pseudo first-order model, pseudo second-order reaction rate model [26 - 29]. The mathematical representations of models are given in Eqs. (3) and (4).

Pseudo first-order adsorption kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The adsorption rate constant ( $k_1$ ) were calculated from the slope of the linear plot of  $\ln(q_e - q_t)$  versus time.

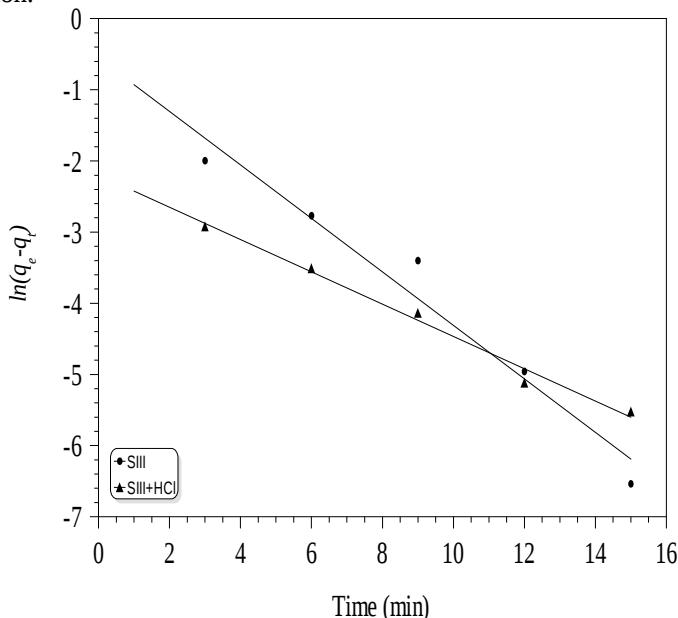
Pseudo second-order adsorption kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Kinetic data were plotted between  $t/q_t$  against  $t$ .

Adsorption kinetics were measured for Cd(II), a typical metal ion by SIII, R400 in absence and presence of 0.005M hydrochloric acid solution.. Since the equilibrium was attained within 15 min, a period of 3 h was considered to be sufficient for the subsequent batch tests.

The rate constant for sorption of Cd(II) was studied by Lagergren rate equation and pseudo-second-order [30] models for initial cadmium concentration of 10 mg/L. Figs. 2–5 show the plot of the first-order, second-order for adsorption of cadmium metal ion by SIII, R400 in absence and presence of 0.005M hydrochloric acid solution.



**Fig. 2. Linear fitting curves of  $\ln(q_e - q_t)$  versus  $t$  for the cadmium ions adsorption onto SIII rice in absence and presence of 0.005 M HCl at 25°C**

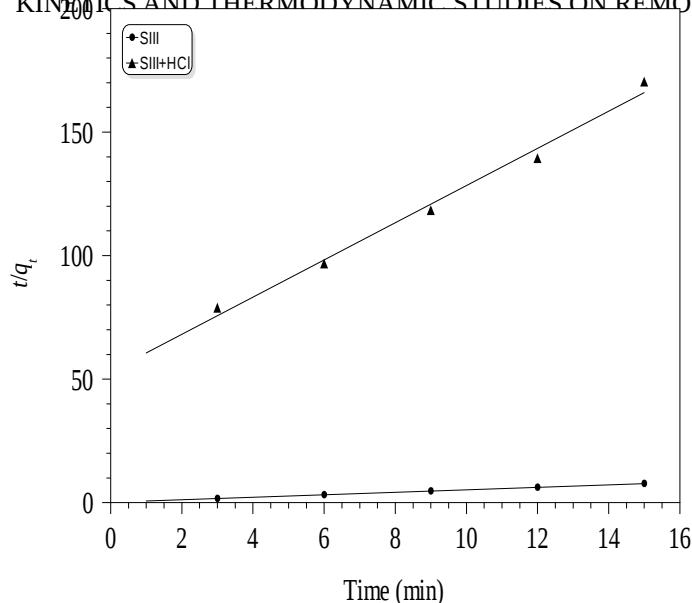


Fig. 3. Linear fitting curves of  $t/q_t$  versus  $t$  for the cadmium ions adsorption onto SIII rice in absence and presence of 0.005 M HCl at 25°C

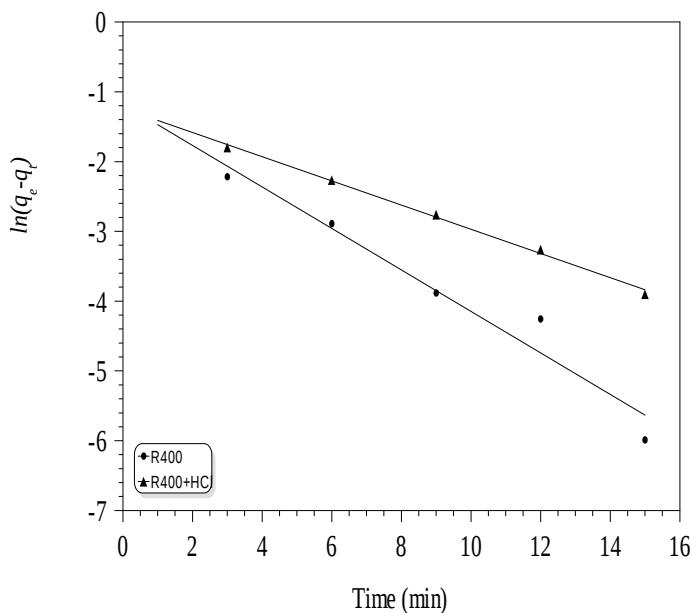
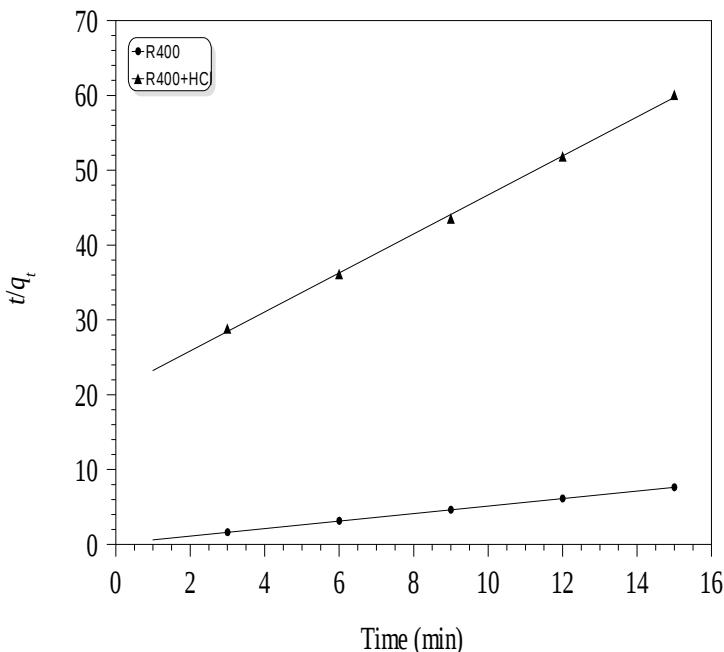


Fig. 4. Linear fitting curves of  $\ln(q_e - q_t)$  versus  $t$  for the cadmium ions adsorption onto ignited 400 rice in absence and presence of 0.005 M HCl at 25°C.



**Fig. 5. Linear fitting curves of  $t/q_t$  versus  $t$  for the cadmium ions adsorption onto ignited .400 rice in absence and presence of 0.005 M HCl at 25°C**

The parameters of the two equations were tabulated in Table 2. The goodness of conformity between experimental data and the model-predicted values was expressed by the coefficient of determination ( $r^2$ ). It can be seen from the results listed in Table 2 As can be seen from the results, the correlation coefficients were low ( $r^2 < 0.99$ ). Also  $q_e$  values calculated from the plots were lower than the experimental data. Therefore, it may conclude that cadmium adsorption did not follow pseudo-first-order equation. It is evident from the results of second-order model that the correlation coefficients for Cd are very high and appeared to be the best-fitting model ( $r^2 > 0.99$ ).

The fitting curves for the adsorption of Cd(II) by second-order equation were shown in Figs. 3, 5. The calculated amount of equilibrium adsorption capacity was similar to the actual tested adsorption capacity. The adsorption rate was related to the content of active adsorption site on the matrix of adsorbent.

**Table 2.** Comparison of the pseudo-first-order, and pseudo-second-order calculated and experimental  $q_e$  values at 25°C.

|                                 | Pseudo-first order                    |                                       |                               |                    | Pseudo-second order |                                       |  |                    | $r^2$  |
|---------------------------------|---------------------------------------|---------------------------------------|-------------------------------|--------------------|---------------------|---------------------------------------|--|--------------------|--------|
|                                 | $q_{e, exp}$<br>(mg g <sup>-1</sup> ) | $q_{e, cal}$<br>(mg g <sup>-1</sup> ) | $k_f$<br>(min <sup>-1</sup> ) | $T_{1/2}$<br>(min) | $r^2$               | $q_{e, cal}$<br>(mg g <sup>-1</sup> ) | $k_2$<br>(g mg <sup>-1</sup> min <sup>-1</sup> ) | $t_{1/2}$<br>(min) |        |
| SIII                            | 1.947                                 | 0.575                                 | 0.3758                        | 1.84               | 0.9607              | 1.986                                 | 0.1637   | 0.31               | 0.9999 |
| 0.005M HCl<br>SIII <sup>+</sup> | 0.092                                 | 0.111                                 | 0.2272                        | 3.05               | 0.9873              | 0.133                                 | 0.1067   | 7.06               | 0.9896 |
|                                 | 1.973                                 | 0.308                                 | 0.2970                        | 2.33               | 0.9531              | 1.999                                 | 0.2152   | 0.23               | 0.9999 |
| 0.005M HCl<br>R400 <sup>+</sup> | 0.270                                 | 0.291                                 | 0.1735                        | 4.00               | 0.9961              | 0.384                                 | 0.0329   | 7.92               | 0.9990 |

### Adsorption mechanisms

The Lagergren first-order and pseudo-second-order models cannot identify the diffusion mechanism. For this reason, the kinetic results were then subjected to analyze by the intraparticle diffusion model. According to this model, the plot of uptake,  $q_t$ , versus the square root of time ( $t^{1/2}$ ) should be linear if the intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. The initial curved portion of the plots seems to be due to boundary layer adsorption and the linear portion to intraparticle diffusion, with the plateau corresponding to equilibrium [31–34].

Intraparticle diffusion model is of major concern because it is rate-determining step in the liquid adsorption systems. During the batch mode of operation, there was a possibility of transport of sorbate species into the pores of sorbent, which is often the rate controlling step.

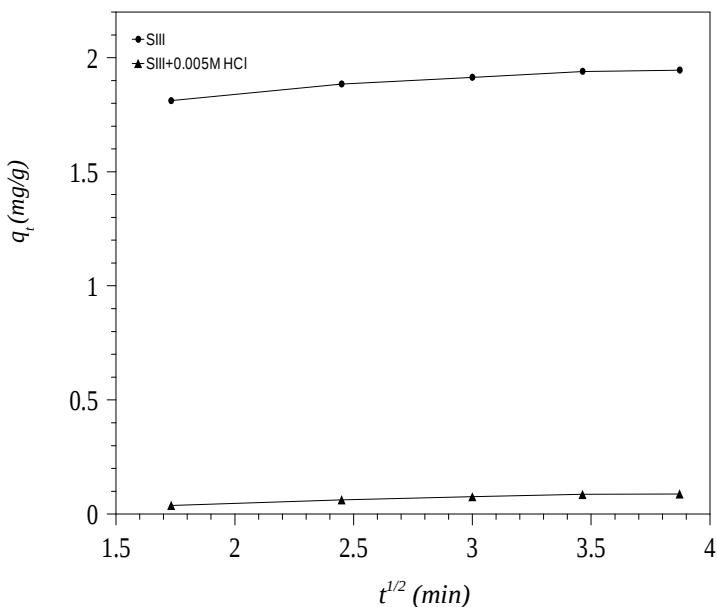
The rate constants of intraparticle diffusion ( $k_{id}$ ) at different temperatures were determined using the following equation:

$$q_t = k_{id} t^{1/2} \quad (5)$$

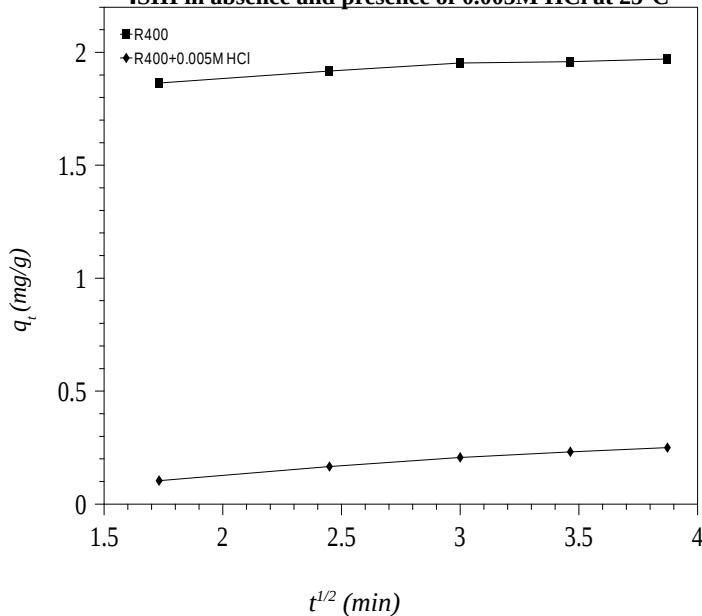
where  $q_t$  is the amount sorbed at time  $t$  and  $t^{1/2}$  is the square root of the time.

When the metal ion solution is mixed with the adsorbent, transport of the metal ions from the solution through the interface between the solution and the adsorbent occurs into pores in the particles.

There are four main stages in the process of adsorption by porous adsorbents [35]: (i) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent's surface, (ii) solute transport from the boundary film to the adsorbent's surface, (iii) solute transfer from the adsorbent's surface to active intraparticulate sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent. One or more of these four steps controls the rate at which solute is adsorbed. The first and second steps were very slow and were found to be the rate-determining step. Figs. 6,7 illustrates the diffusion of cadmium metal ion within rice straw, R400 in absence and presence of 0.005M hydrochloric acid as a function of time and shows that intraparticle diffusion occurred in two stages.



**Fig. 6. Weber and Morris (intraparticle diffusion) plot for the adsorption of Cd(II) by .SIII in absence and presence of 0.005M HCl at 25°C**



**Fig. 7. Weber and Morris (intraparticle diffusion) plot for the adsorption of Cd(II) by .R400 in absence and presence of 0.005M HCl at 25°C**

The cadmium metal ions diffused quickly among the particles at the beginning of the adsorption process, and then intraparticle diffusion slowed down and stabilized. The deviation of these lines from the origin (i.e., a *y*-intercept other than 0), in SIII and R400, indicates that intraparticle transport is not the only rate-limiting step. It can be assumed that external mass transfer controls the rate of adsorption because of the very slow transfer speeds.

#### Adsorption Thermodynamics

Thermodynamic parameters, including Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) were used to decide whether the adsorption process is spontaneous or not.  $\Delta G^\circ$  were calculated from the following equation;

$$\Delta G^\circ = -RT \ln K_D \quad (6)$$

where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the temperature (K), and  $K_D$  is the distribution coefficient. The  $K_D$  value was calculated using following equation [36];

$$K_D = \frac{q_e}{C_e} \quad (7)$$

where  $q_e$  and  $C_e$  are the equilibrium concentration of metal ions on adsorbent ( $\text{mg L}^{-1}$ ) and in the solution ( $\text{mg L}^{-1}$ ), respectively. Relation between  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  can be expressed by the following equation;

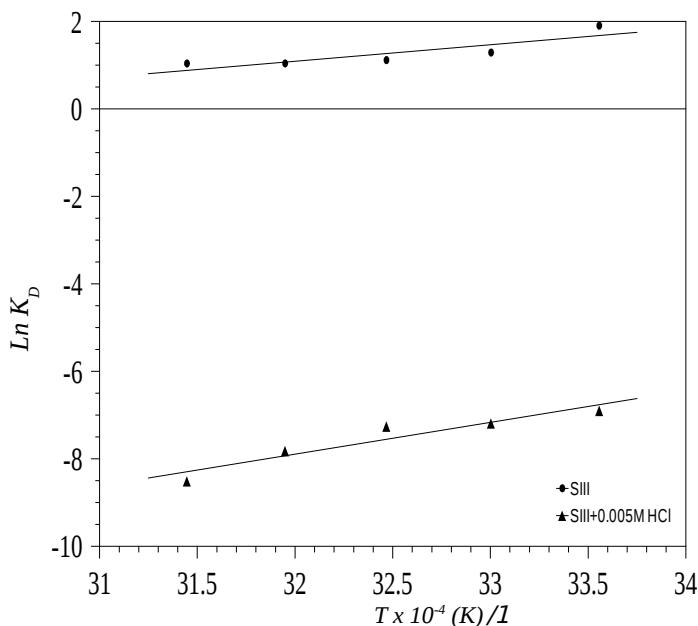
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

This equation can be written as;

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Thermodynamic parameters,  $\Delta H^\circ$  and  $\Delta S^\circ$ , were calculated from the slope and intercept of the plot of  $\ln K_D$  versus  $1/T$ , respectively.

The effect of temperature on the adsorption of cadmium metal ions onto SIII, R400 in absence and presence of 0.005M hydrochloric acid solution are given from the plots and curves of the distribution coefficient values  $K_D$  versus temperatures in Fig. 8. It can be found that  $K_D$  slightly decreased with temperature increasing, a certification of the exothermic adsorption nature.



**Fig. 8. Van't Hoff plot of adsorption equilibrium constant  $K_D$  of cadmium metal ion on SIII .in absence and presence of 0.005M HCl**

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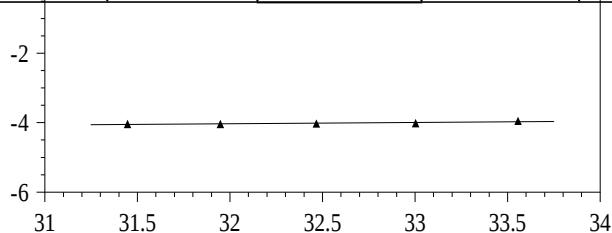
Thermodynamic parameters including free energy change ( $\Delta G_o$ ), enthalpy change ( $\Delta H_o$ ) and entropy change ( $\Delta S_o$ ) are respectively estimated in Table 3. The negative values of  $\Delta H_o$  represent the exothermic natures of adsorption processes. According to Alkan et al. [37], enthalpy change due to chemisorption takes value between 40 and 120 kJ mol<sup>-1</sup>, which is larger than that due to physisorption. Therefore, the low value of heat of adsorption obtained in this study indicates that adsorption is likely due to physisorption.

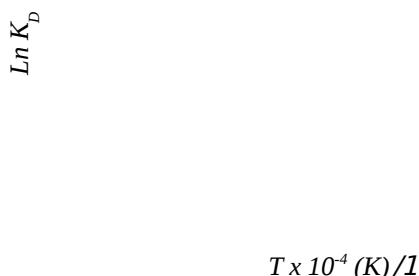
The negative values of  $\Delta G_o$  confirm the feasibility of the process and the spontaneous nature of adsorption of Cd(II) onto SIII, R400.

All of entropy change values  $\Delta S_o$  are negative except in R400, shows a decreased disorder at the solid/liquid interface during cadmium adsorption. The positive  $\Delta S_o$  value in R400 corresponds to an increase in the degree of freedom of the adsorbed species [36].

**Table 3. Thermodynamic parameters of the adsorption of cadmium metal ions by SIII and R400 in absence and presence of 0.005M HCl.**

|                          | Temp (K) | K <sub>D</sub> | $\Delta H_o$<br>(kJ/mole) | $\Delta S_o$ (J/mole) | $\Delta G_o$<br>(kJ/mole) |
|--------------------------|----------|----------------|---------------------------|-----------------------|---------------------------|
| SIII                     | 298      | 6.694          | -31.5319                  | -90.01                | -4.71                     |
|                          | 303      | 3.617          |                           | -93.38                | -3.24                     |
|                          | 308      | 3.041          |                           | -93.13                | -2.85                     |
|                          | 313      | 2.821          |                           | -92.12                | -2.70                     |
|                          | 318      | 2.817          |                           | -90.55                | -2.74                     |
| SIII +<br>0.005M HCl     | 298      | 0.0010         | -60.4361                  | -260.20               | 17.10                     |
|                          | 303      | 0.0008         |                           | -259.25               | 18.12                     |
|                          | 308      | 0.0007         |                           | -256.59               | 18.59                     |
|                          | 313      | 0.0004         |                           | -258.12               | 20.36                     |
|                          | 318      | 0.0002         |                           | -260.85               | 22.52                     |
| R400                     | 298      | 47.647         | -5.1490                   | 14.85                 | -9.57                     |
|                          | 303      | 45.546         |                           | 14.76                 | -9.62                     |
|                          | 308      | 44.403         |                           | 14.82                 | -9.71                     |
|                          | 313      | 43.459         |                           | 14.91                 | -9.82                     |
|                          | 318      | 41.423         |                           | 14.77                 | -9.85                     |
| R400 +<br>0.005 M<br>HCl | 298      | 0.0193         | -3.1793                   | -43.49                | 9.78                      |
|                          | 303      | 0.0181         |                           | -43.84                | 10.10                     |
|                          | 308      | 0.0179         |                           | -43.76                | 10.30                     |
|                          | 313      | 0.0177         |                           | -43.69                | 10.50                     |
|                          | 318      | 0.0177         |                           | -43.55                | 10.67                     |





**Fig. 9. Van't Hoff plot of adsorption equilibrium constant  $K_D$  of cadmium metal ion .on R400 in absence and presence of 0.005M HCl**

### Conclusion

In this study, batch adsorption experiments for the removal of Cd(II) from aqueous solutions have been carried out using rice straw and its ash, readily available natural adsorbents. The adsorption characteristics have been examined in presence and absence of 0.005M HCl. The obtained results can be summarized as follows:

1. Cd showed higher adsorption capacity and rate in absence of hydrochloric acid solution.
2. Experimental data were represents the adsorption kinetics fit to pseudo-second order model as evident from correlation coefficient values ( $r^2$ ).
3. Adsorption free energy showed that the Cd(II) adsorption were spontaneous in absence of hydrochloric acid solution.
4. Enthalpy of adsorption showed that the Cd(II) adsorption were exothermic in absence and presence of 0.005M hydrochloric acid solution.
5. Rice straw and its ash can be used as an effective natural biosorbent for the economic treatment of wastewater containing Cd(II).

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