

Adsorption of Selenium From Aqueous Solution by Rice Husk : Characterization , Isotherm and Kinetic Studies

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ABSTRACT

The present study explores the adsorption potential of rice husk to remove selenium from aqueous solution. The presence of -OH , -NH ,and -CO groups play major role in adsorption of selenium ions onto adsorbent . The surface morphology pretends to be porous in nature. The optimum equilibrium time and pH was 120 min and 4.0. The adsorption isotherm fitted best was Temkin. The monolayer adsorption capacity of rice husk was 0.810 mg/g. The adsorption data was best fitted by pseudo- second order kinetics with regression coefficient of 0.997 and liquid film diffusion model was rate controlling step. The positive value of ΔH and ΔS suggest that the process was endothermic and randomness at solid - solution interface.

Keywords: Rice Husk, Selenium, Adsorption, Temkin.

I. INTRODUCTION

Tremendous increase in the use of heavy metals over the last few decades has inevitably resulted in an increased flux of metallic substances into the aquatic environment. Acid mine drainage, industrial and domestic effluents, agricultural runoff, acid rain and so forth have all contributed to the metal loads in water bodies. The heavy metals are hazardous to humans include copper, zinc, nickel, lead, mercury, cadmium, arsenic, chromium and selenium [1]. Selenium plays a vital role in the biological functions of humans, animals and plants in the range 0.8 – 1.7 micro mol / litre. Beyond this range it becomes toxic [2]. It is found in organic and inorganic forms in the environment. Its concentration has been increasing in the environment due to its several industrial applications such as oil refineries, thermal power stations, smelting plants, solar panels, semi conductors and glass production [3]. In India several incidents of chronic selenium toxicity in animals have been reported. Selenium poisoning in domestic buffaloes in the Karnal area of the North West plain of India has been reported. High Selenium levels found in the animals are attributed to the readily available selenium in the alkaline soils of the regions. Selenium is leached from the soil by irrigation water in the paddy fields and is taken up by the rice plants, which accumulates it to toxic levels in the straw. This is

the main fodder of the animals after harvest and is immediate cause of the toxicity. A similar pattern of mobilization of naturally occurring selenium caused by paddy field irrigation that also resulted in poisoning of domestic animals in Southern India[4]). The typical concentration of selenium in waste water is always more than the 0.05 mg/l and generally around 0.01 mg/l. Because of its high toxicity, the USEPA has proposed a standard of 0.05 mg/l for drinking water. For inland surface water, public sewers and marine / coastal areas, the Central Pollution Control Board (CPCB), Delhi, India has set a standard of 0.05 mg/l.

Numerous appropriate methods, including chemical precipitation, ion exchange and catalytic reduction have been used in the removal of selenium from aqueous media when it is present in higher concentrations [5]. On the other hand selenium is very difficult and expensive to remove where it is present at very low concentrations. The permissible level of selenium in drinking water is 10 $\mu\text{g/L}$ [6]. Therefore, at even very low concentrations of selenium in water, it is toxic. For this reason, it is essential to develop economic and eco friendly methods for the removal of selenium ions from aqueous samples. Adsorption using naturally existing plant biomass as a adsorbent either in direct or modified form is always superior to the conventional adsorbents in terms of cost, availability and

efficiency [7]. In our earlier studies various types of low cost adsorbents like *Hydrilla verticillata*, *Eichhornia crassipes*, *Lemna minor*, Iron- oxides based nano particles were used for the removal of dye/metals from aqueous solution [8 ,9]

In the present work Rice husk (an agricultural waste) has been utilized as a potential adsorbent for the treatment of selenium from aqueous solution, by systematic evaluation using a set of parameters like pH, concentration, time and temperature. The resultant data were examined using pseudo - first order, pseudo – second order, intra particle diffusion, liquid film diffusion and elovich equation. Isotherm studies and thermodynamic behaviour of adsorption were also evaluated.

II. METHODS AND MATERIAL

Stock solution of sodium selenite in distilled water, EDTA, FeCl₃, Triethanol amine, methylene blue, Na₂S.9H₂O, Na₂SO₃ and NaOH. All the reagents were of analytical grade.

ADSORBENT PREPARATION :

The Rice Husk of 500g was collected from Ganga – Gayatri rice mill, industrial area, Naini, Allahabad. The adsorbent was washed with water and dried in sun light for 3 days and then ground to a size of 400 μm.

BATCH ADSORPTION STUDY :

The adsorption studies were carried out in batch process. Solution of metal of desired concentration (1 mgL⁻¹) were equilibrated with 1 gm of adsorbent at room temperature. Each experiment was carried out by adding 6.5 ml of sample solution, 1 ml formaldehyde, 2.5 ml of conditional solution, 0.5 ml of sodium sulphide solution and 1 ml methylene blue solution into a beaker and agitated at 170 rpm. The samples were taken at different time intervals of (30, 60, 90, 120, 150 and 180) and were filtered after 120 min. The selenium ion in the solution was then analysed by spectrophotometer. The effect of solution pH was analysed in the range (2 – 10). The initial metal ion concentration was determined between (1 – 6 mgL⁻¹). The adsorption efficiency (%) and capacity of the adsorbent were calculated from the formula.

$\% \text{ removal} = (C_0 - C_e)/C_0 \times 100$ $q_e = (C_0 - C_e)/W \times V$
 where C₀ is the initial metal ion concentration (mg L⁻¹),
 C_e is the final metal ion concentration (mg L⁻¹), q_e is

the adsorption capacity (mg g⁻¹). W is the weight of the adsorbent in g, and V is the volume of metal ion solution (L).

III. RESULTS AND DISCUSSION

CHARACTERIZATION:

Figure. 1(a) shows the morphology of rice husk exhibits a porous and amorphous structure before adsorption. Figure 1(b) exhibits that the pores have been occupied by selenium ion after adsorption.

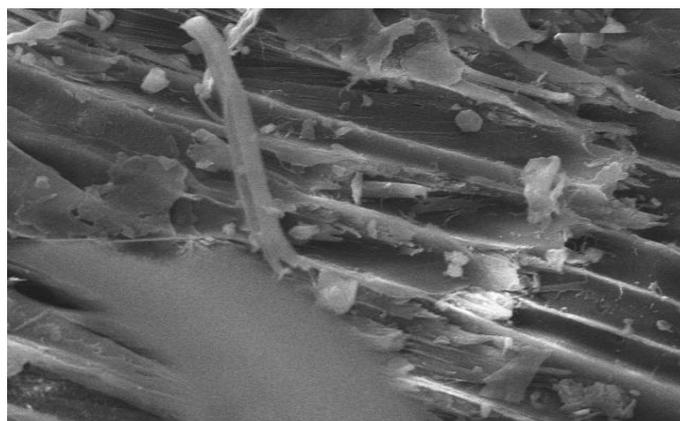


Figure 1(a). SEM analysis before adsorption

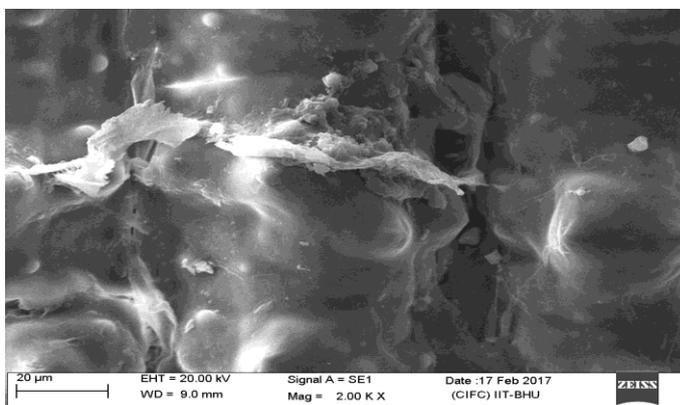


Figure 1(b). after selenium adsorption.

FTIR Spectra of rice husk:

The FTIR spectra for selenium adsorption before and after adsorption are shown in Figure 2 (A) and Figure 2 (B). In Rice husk the peaks at 3429.61 corresponds to OH group due to adsorbed water and silanol group. The peaks at 1637.41 corresponds to –C= O stretching of carbonyl group. The peaks at 1260.79 and 800.15 are due to C-O stretching of ester group and C -Cl stretching of alkyl halide [10]. The peaks at 1092.46 is

due to C – N stretching of aliphatic amines. After adsorption the peaks shifted from 3429 to 3424 due to both the silanol group (Se – OH) and adsorbed water on the surface. The shifts from 1092.46 to 1096.13 is due to C – N stretching reflects the interaction between amino group and metal ion [11].

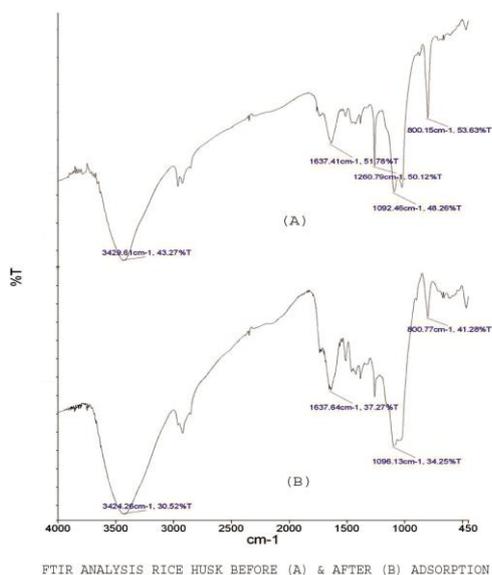


Figure 2. FTIR analysis before (A) and after (B) selenium adsorption.

3.2 EFFECT OF CONTACT TIME :

The contact time was studied in the range of 30–180 min at 25°C at pH 4 and initial concentration of 1 mg L⁻¹ (Figure 3). This shows a very fast adsorption in the beginning and then slows down. The adsorption equilibrium was attained in 120 min and the maximum adsorption capacity was found to be 0.0111 mg/g. After this period the amount of metal ions adsorbed did not change significantly with time. The rapid uptake of metal ions on the adsorbent indicate that most of reaction sites of the adsorbent were exposed for interaction with metal ion [12].

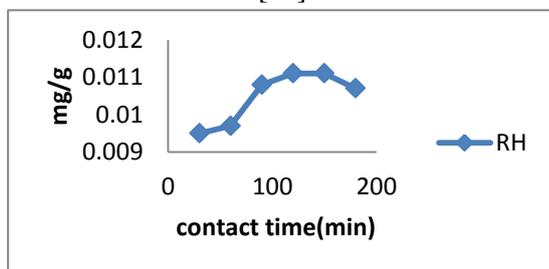


Figure 3. Effect of contact time on adsorption of selenium.

3.3 EFFECT OF pH :

The pH plays an important role in the adsorption process by affecting the surface charge of the adsorbent. The effect of pH was studied at different pH range (2 – 10) (Figure 4). The maximum uptake was observed at pH 4, after that it tends to decrease due to the formation of hydroxide of metal ion [13]. At a lower pH, there is more competition of H⁺ and metal ions for the available biosorption sites. However as pH increases, this competition decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction [14].

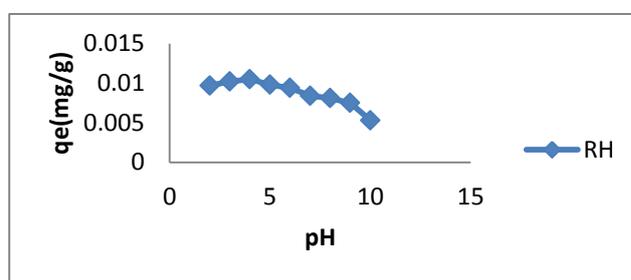


Figure 4. Effect of pH on the adsorption of selenium.

3.4 ADSORPTION ISOTHERMS :

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Adsorption isotherm can be generated based on theoretical models were Langmuir and Freundlich models are the most commonly used [15]. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The linear form of Langmuir isotherm equation is given (16)

$$1/q_e = 1/b \cdot q_m + 1/q_m \cdot 1/c_e \quad (3)$$

Where q_e is the equilibrium capacity of selenium on the adsorbent (mg/g), C_e is the equilibrium concentration, of the selenium solution (mg/L). q_m is the monolayer adsorption capacity of adsorbent (mg/g) and b is the Langmuir constant (L/mg) which is related to free energy of the adsorption. A plot of $1/q_e$ Vs $1/C_e$ is shown in Figure – 5 and values obtained are in table – 1.

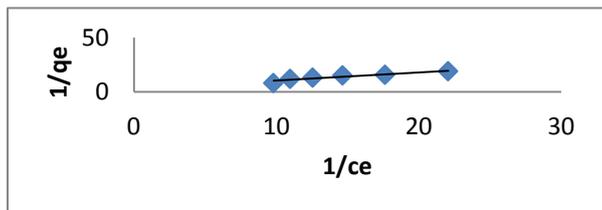


Figure 5. Langmuir adsorption isotherm for adsorption of selenium.

Freundlich isotherm is applied for multilayer adsorption or heterogeneous adsorbent and it is assumed that adsorption sites increases exponentially to heat to adsorption and Freundlich equation is an empirical equation. The linear form of Freundlich equation is given as: [17]

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{---} \quad 4n$$

where K_f (lg^{-1}) and n are Freundlich constant of system. The values of n should lie between 0 and 10 for the favourable adsorption process. The plot of $\log q_e$ Vs $\log C_e$ is shown in Figure 6 and values of constants and correlation coefficient (R^2) are shown in table – 1. The values of R^2 and n predict the feasibility and favourability of adsorption isotherm.

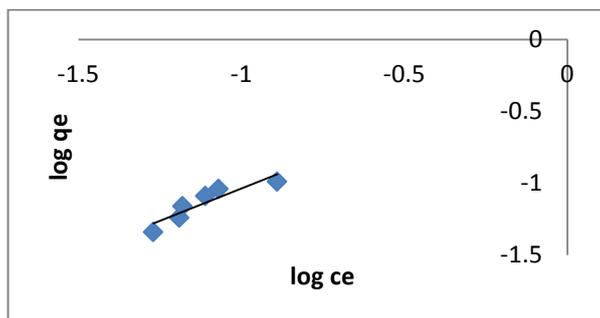


Figure 6. Freundlich adsorption isotherm for the removal of selenium.

Temkin adsorption isotherm:

Heat of adsorption and adsorbent – adsorbate interaction on adsorption isotherm were studied by Temkin and Pyzhev (1940). The linearized form of equation is [18]

$$q_e = B_1 \ln k_1 + B_1 \ln C_e \quad (5)$$

Where $B_1 = RT/b$, T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J/mol K), k_1 is the equilibrium binding constant (L/mg) and B_1 is related to the heat of adsorption. A plot of q_e Vs $\ln C_e$ is shown in Figure 8 and values of constants are given in table 1.

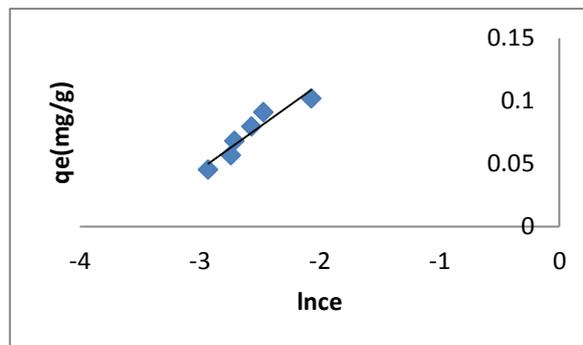


Figure 7. Temkin adsorption isotherm for the removal of selenium

The Dubinin – Radushkevich isotherm (D – R) is more general than Langmuir isotherm because it does not assume a homogeneous surface or constant sorption potential. The (D – R) equation is described as [19]

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (7)$$

where β is the constant related to the mean free energy of the adsorption per mole of the adsorbate ($\text{mole}^2 / \text{KJ}^2$), q_m is the theoretical saturation capacity and ϵ is the polanyi potential, which is equal to $RT \ln (1 + 1/C_e)$ where R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant and T is the absolute temperature. The values of q_m , β and R^2 are calculated from the plot of $\ln q_e$ vs ϵ^2 and tabulated in table 1. The adsorption isotherm studies showed that the process was chemical in nature.

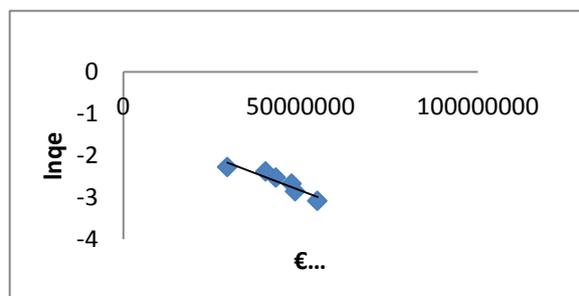


Figure 8. D-R adsorption isotherm for the removal of selenium.

Table 1. Adsorption isotherm of Rice Husk for selenium

S. No.	Parameter	Rice Husk
1.	Langmuir Isotherm	
	Q_m	0.810
	b	-0.636
	R^2	0.878
2.	Freundlich Isotherm	
	K_f	0.739

	1/n R ²	0.904 0.829
3.	Temkin Isotherm B ₁ K _T R ²	0.068 1.29 0.896
4.	D – R Isotherm β Q _m R ²	- 3 x 10 ⁻⁸ 3.36 0.877

The calculated results of Langmuir, Freundlich, Temkin and D – R isotherms are given in table 1. Isotherm studies show that the data is best correlated with Temkin isotherm.

3.5 ADSORPTION KINETICS :

Controlling mechanism of adsorption was examined by the pseudo first order, pseudo – second order and intra – particle diffusion model. The pseudo – first order was given by [20]

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (8)$$

where q_t and q_e are the uptake capacity of biosorption at time t and at equilibrium in mg/g and t is the time in min. and k_1 is the rate constant of the equation in min^{-1} .

The pseudo – second order model predict the behaviour over the whole adsorption process. This model assumes that the two reactions are occurring, the first one is fast and second is the slower process may be series or in parallel. The linear form of equation is given by HO McKay :

$$t/q_t = 1/q_e^2/k_2 + t/q_t \quad (9)$$

where q_t is the uptake capacity of biosorption at time t in mg/g and q_e is the uptake capacity of adsorption at equilibrium in mg/g, and k_2 is the rate constant in $\text{g mg}^{-1} \text{min}^{-1}$.

A plot of t/q_t Vs t is shown in figure 10.

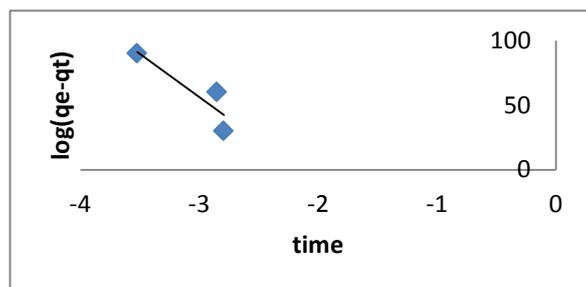


Figure 9. Pseudo - first order kinetics for adsorption of selenium

From the table R² values for pseudo -second order is higher as compared to pseudo – first order kinetics and therefore the data are best followed by pseudo- second order kinetics.

The kinetic data were analyzed by intra-particle diffusion model to elucidate the diffusion mechanism [21]

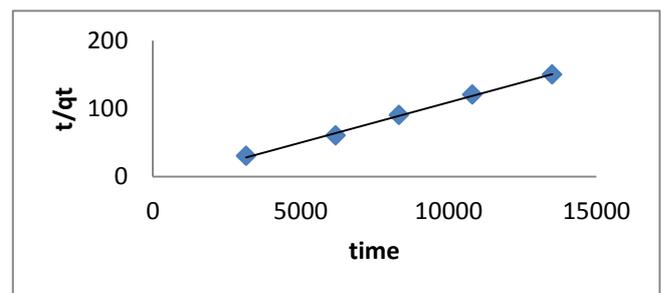
$$q_t = K_{id}t^{1/2} + C \quad (10)$$

where K_{id} ($\text{mg/g min}^{-1/2}$) is the intra particle diffusion constant and q_t is the adsorption capacity at time t (mg/g). The values of K_{id} , C and R^2 were calculated from slope of plot q_t vs $t^{1/2}$ in fig. 11 From the table the value of K_{id} is zero means, intra particle diffusion model which is applicable at slow process of adsorbate flow through the liquid film surrounding the adsorbent particles. The equation for liquid film diffusion model is given by [22]

$$\ln (1 - F) = -K_{fd} t \quad (11)$$

$$\text{where } F = Q_t/Q_e \quad (12)$$

F is the fractional attainment at equilibrium and K_{fd} is the film diffusion rate constant. Plot of $\ln (1 - F)$ Vs t with zero intercept suggest that adsorption kinetics is controlled by diffusion through liquid film surrounding the solid adsorbents. The close to unity value of R^2 indicated the best fit of liquid film diffusion model.



The adsorption data were further analysed with Elovich equation (23)

$$q_t = A + B \ln t \quad (13)$$

A and B are Elovich constants. The values of A , B and R^2 are calculated from the plot of Fig. 13 are given in table 2 showed that experimental data is best followed by pseudo- second order equation.

Figure 10 Pseudo - second order equation for the removal of selenium.

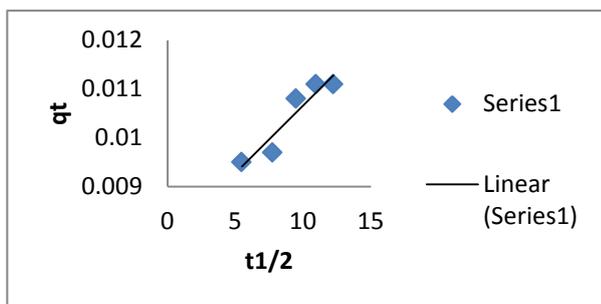


Figure 11. Intra particle diffusion for the adsorption of selenium.

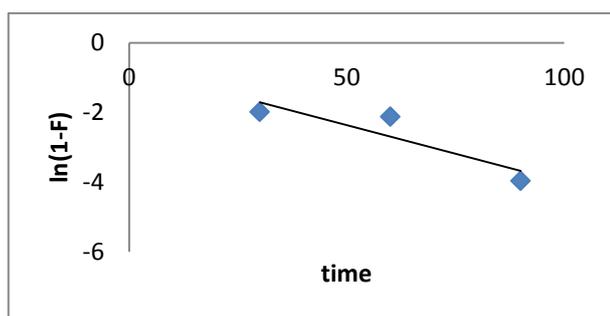


Figure 12. Liquid film diffusion model for the adsorption of selenium.

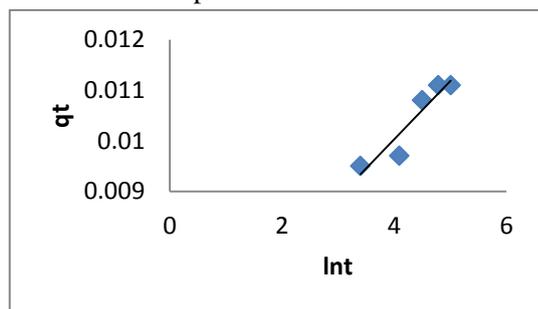


Figure 13. Elovich model for the adsorption of selenium

3.6 THERMODYNAMIC STUDIES:

The effect of temperature on the adsorption of selenium was studied in the range 298K - 328K by using rice husk. The different thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 were calculated by using the relation [24]

$$K_C = C_s/C_e \quad (14)$$

$$\Delta G^0 = -RT \ln K_C \quad (15)$$

$$\log K_C = \Delta S^0/2.303R - \Delta H^0/2.303RT \quad (16)$$

where K_C is the equilibrium constant, C_s is solid phase concentration at equilibrium (mg/L), C_e is the equilibrium concentration in solution (mg/L). The values of ΔH^0 and ΔS^0 are obtained from slope and

intercept of the plot $\log K_C$ versus $1/T$ as shown in fig. 14 and presented in table 3. The negative value of ΔG^0 confirmed that the process was spontaneous and thermodynamically favourable at high temperature. The positive value of ΔH^0 and ΔS^0 indicate the endothermic nature and randomness at solid liquid interphase during adsorption of selenium on rice husk.

Table 2. Kinetic Parameters

S. No.	Parameters	Rice Husk
1.	Pseudo – first order K_1 q_e (Cal.) q_e (Exp.) R^2	0.027 4.68 0.011 0.809
2.	Pseudo – Second Order K_2 q_e (Cal.) q_e (Exp.) R^2	9.803 0.011 0.011 0.997
3.	Intra Particle diffusion K_{id} C R^2	0 0.007 0.891
4.	Liquid Film Diffusion K_{fd} Intercept R^2	0.026 -0.92 0.802
5.	Elovich Equation A B R^2	0.001 0.005 0.883

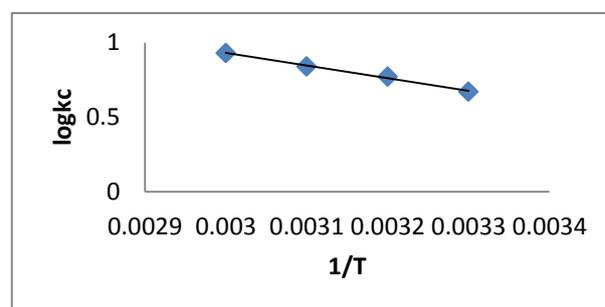


Figure 14. plot of $\log k_c$ vs $1/T$ for the adsorption of selenium

Table 3. Thermodynamics parameters of selenium onto rice husk

Temp. (°C)	ΔG^0 (KJ /mol)	ΔH^0 (KJ /mol)	ΔS^0 (KJ /mol)	R^2
25	-3.71	15.86	0.065	0.9
35	-4.53			97
45	-5.12			
55	-5.86			

Adsorbent Comparative Study:

To evaluate the feasibility and absorptive capacity with other adsorbents a comparative study is been shown in table 4.

Adsorbents	Adsorptive Capacity(mg/g)	References
<i>Aspergillus sp.</i>	6.31	[23]
<i>Iron oxide coated sand</i>	1.34	[24]
<i>Aluminium oxide coated sand.</i>	1.08	[25]
<i>Wheat bran</i>	0.0892	[26]
<i>Rice husk ash</i>	0.283	[4]
<i>Rice husk</i>	0.810	Present study

IV. CONCLUSION

The present study demonstrates the possible application of rice husk for the removal of selenium. The maximum adsorption was obtained at pH 4.0. The equilibrium was attained in 120 min. It is concluded that Temkin isotherm is best fitted isotherm with higher R^2 value.

The kinetic data showed the pseudo – second order and liquid film diffusion fitted well.

The positive value of ΔH^0 indicated that process to be endothermic and spontaneous with randomness at solid liquid solutions interface.

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