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Removal of selenium from waste water by sweet lime peel

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Abstract

The present study explained the adsorption potential of sweet lime peel to remove selenium from aqueous solution. The presence of -OH, -N-H, C=O, -C-O 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 D-R. The monolayer adsorption capacity of sweet lime peel was 1.213. 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: sweet lime peel, Selenium, Adsorption, Diffusion

Introduction

Rapid growth and development of industries, mining and population increases the pressure on the water resources. These 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 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 plantbiomass 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 sweet lime peel 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. Isotherm studies and thermodynamic behaviour of adsorption were also evaluated.

Materials and methods

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 sweet lime peel of 500g was collected from local market, 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 (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).

Results and discussion

Characterization

Fig. 1(a) shows the SEM image of sweet lime peel which has a porous structure with some cavities which increases the surface area of adsorption and Fig. 1(b) exhibits that the pores have been occupied by selenium ion after adsorption

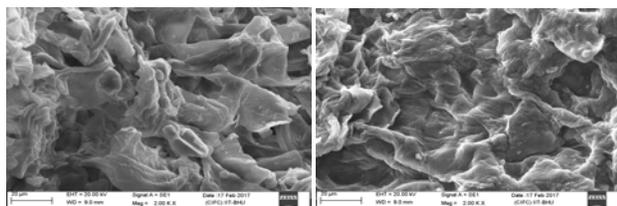


Fig 1: SEM image of sweet lime peel before (a) and after (b) adsorption.

FTIR Spectra of sweet lime peel: The FTIR spectra for selenium adsorption before and after adsorption are shown in Fig. 2 (a) and Fig. 2 (b). In sweet lime peel the peaks at 3412.89 corresponds to OH stretching of hydroxyl group. The peaks at 2923.06 corresponds to aliphatic C-H group. The

peaks at 1736.45 arising from C=O group of carboxylic acids or esters and a peak at 1625.94 arising from stretching of amide group. A distinct peak at 1439.25 is due to symmetrical bending of -CH₃ group. A peak at 1261.85 is due to C-O stretching of acidic group. Moreover the peak at 1070.21 is due to C-O stretching of ether. The peak at 631.30 is due to the presence of alkyl halide. After adsorption the peaks shifted from 3412.89 to 3430.76, 1625.94 to 1633.62, 1070.21 to 1097.98 confirmed the presence of -OH, N-H, C=O, and C-O group in sweet lime peel [11].

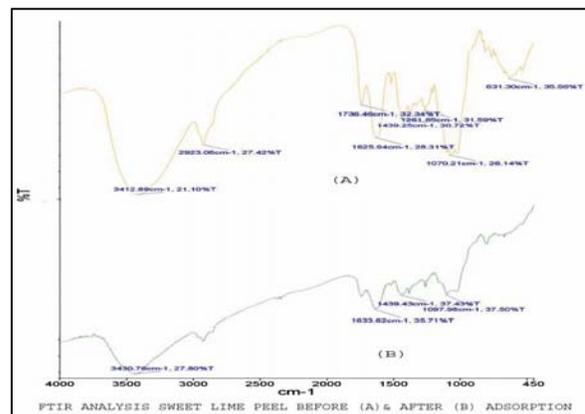


Fig 2: FTIR analysis before (a) and after (b) selenium adsorption.

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 (Fig. 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 0.009 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].

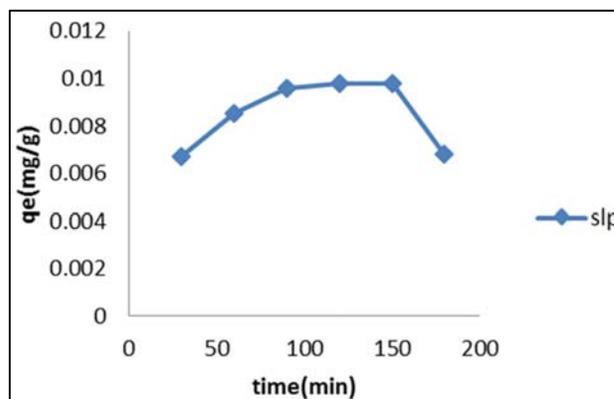


Fig 3: Effect of contact time on adsorption of selenium.

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) (Fig. 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].

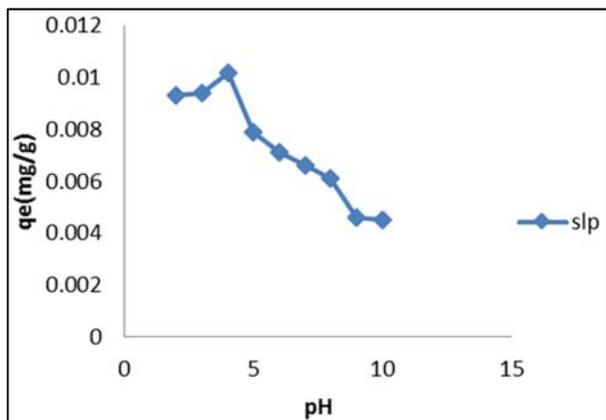


Fig 4: Effect of pH on the adsorption of selenium.

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 Fig. – 5 and values obtained are in table – 1.

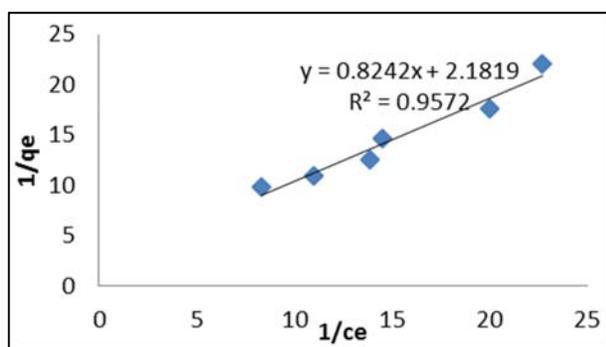


Fig 5: Langmuir adsorption isotherm for adsorption of selenium.

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 a:^[17]

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

where K_f ($l \cdot g^{-1}$) 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 Fig. 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.

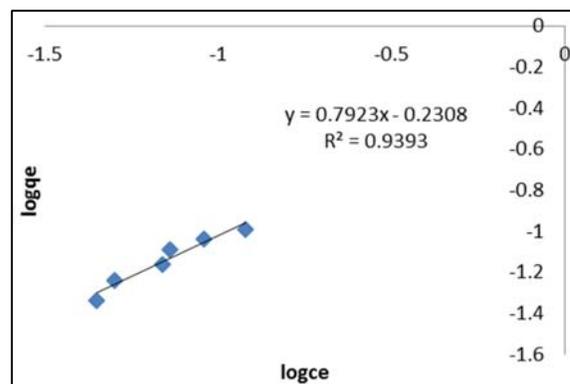


Fig 6: Freundlich adsorption isotherm for the removal of selenium.

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 Fig. 8 and values of constants are given in table – 1.

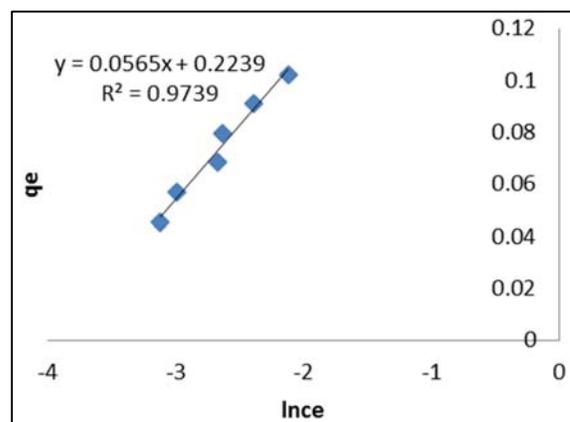


Fig 7: Temkin adsorption isotherm for the removal of selenium.

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 and tabulated in table 1. The adsorption isotherm studies showed that the process was chemical in nature.

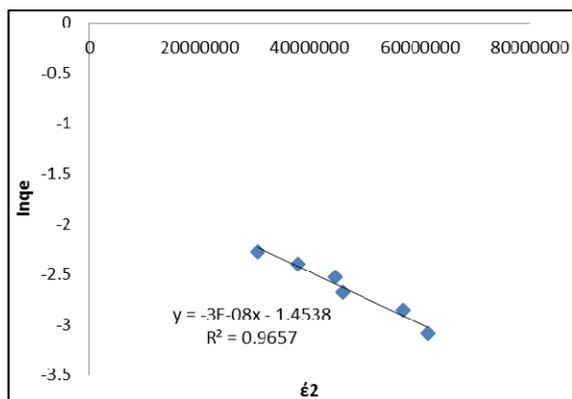

Fig 8: D-R adsorption isotherm for the removal of selenium.

Table 1: Adsorption isotherm of sweet lime peel for selenium.

S. No.	Parameter	Sweet lime peel
1.	Langmuir Isotherm	
	Q_m	1.213
	b	0.378
	R^2	0.957
2.	Freundlich Isotherm	
	K_f	1.733
	$1/n$	0.792
	R^2	0.939
3.	Temkin Isotherm	
	B_1	0.056
	K_T	1.38
	R^2	0.973
4.	D – R Isotherm	
	β	-3×10^{-8}
	Q_m	4.28
	R^2	0.965
	E	14.28

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].

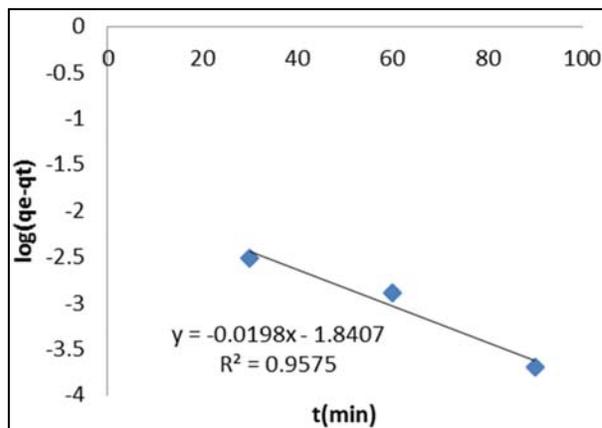
$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (8)$$

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:

$$t/qt = 1/qe^2/k_2 + t/qt \quad (9)$$

where qt is the uptake capacity of biosorption at time t in mg/g and qe is the uptake capacity of adsorption at equilibrium in mg/g, and k_2 is the rate constant in g mg min^{-1} . A plot of t/qt Vs t is shown in fig. 10.


Fig 9: Pseudo - first order kinetics for adsorption of selenium.

From the table R^2 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].

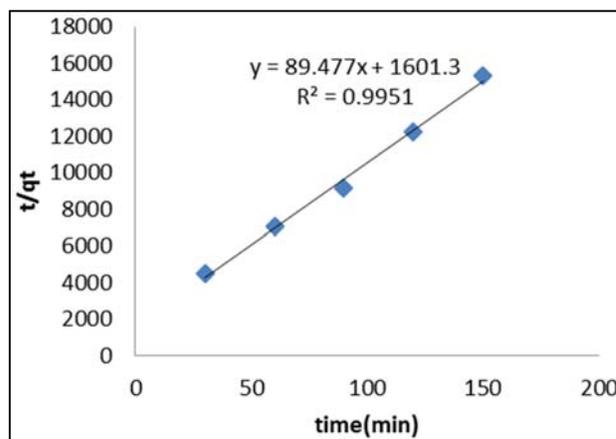
$$q_t = K_{id}t^{1/2} + C \quad (10)$$

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.


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

From the value given in table 2 showed that experimental data is best followed by pseudo- second order equation.

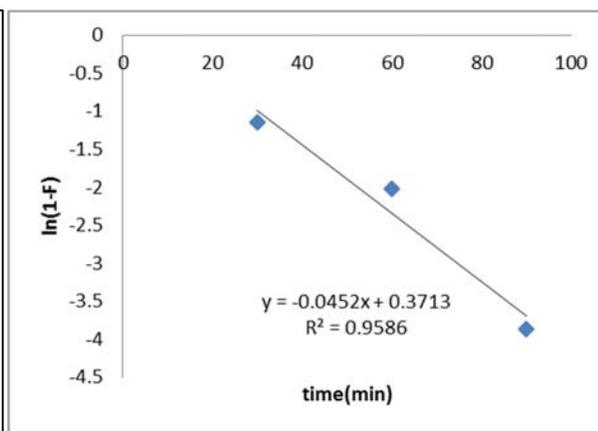
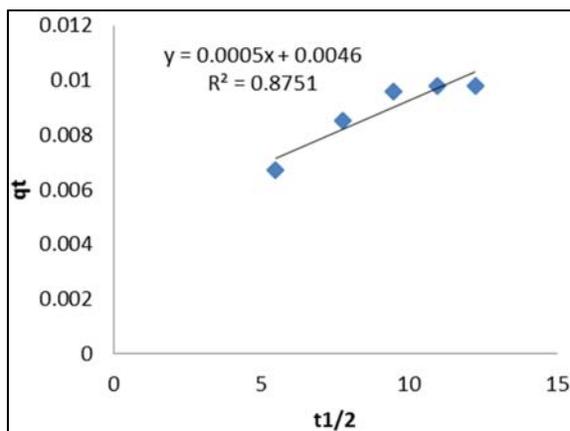


Fig 11: Intra particle diffusion for the adsorption of selenium. Fig 12: Liquid film diffusion model for the adsorption of selenium.

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 ^[11].

$$K_C = C_S/C_e \quad (13)$$

$$\Delta G^0 = -RT \ln K_C \quad (14)$$

$$\log K_C = \Delta S^0/2.303R - \Delta H^0/2.303RT \quad (15)$$

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 sweet lime peel.

Table 2: Kinetic Parameters

S. No.	Parameters	Sweet lime peel
1.	Pseudo – first order	
	K_1	0.043
	q_e (Cal.)	0.014
	q_e (Exp.)	0.009
2.	Pseudo – Second Order	
	K_2	5.16
	q_e (Cal.)	0.011
	q_e (Exp.)	0.009
3.	Intra Particle diffusion	
	K_{id}	0
	C	0.004
	R^2	0.875
4.	Liquid Film Diffusion	
	K_{fd}	0.054
	Intercept	0.752
	R^2	0.931

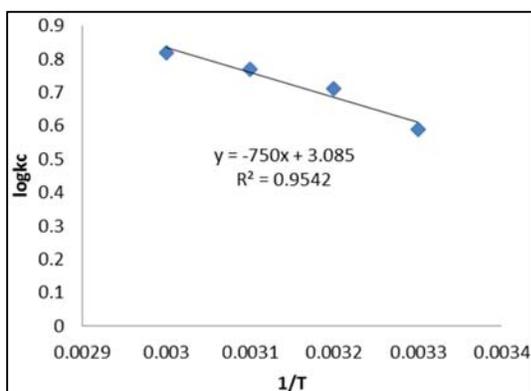


Fig 14: plot of $\log k_c$ vs $1/T$ for the adsorption of selenium.

Table 3: Thermodynamics parameters of selenium onto sweet lime peel.

Temp. ($^{\circ}$ C)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol)	R^2
25	-3.39	14.36	0.059	0.954
35	-4.20			
45	-4.70			
55	-5.18			

Adsorbent Comparative Study

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

Adsorbents	Adsorptive Capacity(mg/g)	References
Aspergillus sp.	6.31	[25]
Iron oxide coated sand	1.34	[26]
Aluminium oxide coated sand.	1.08	[27]
Wheat bran	0.0892	[28]
Rice husk ash	0.283	[4]
Sweet lime peel	1.213	Present study

Conclusion

The present study justified the application of sweet lime peel 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 was the rate controlling step. 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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