ADSORPTION AND KINETIC STUDIES ON REMOVAL OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTION USING TAMARINDUS INDICA AS ADSORBENT

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Abstract: The adsorption of Chromium VI studies were conducted using an adsorbent prepared from tamarindus indica seeds and batch experimental studies were conducted by varying various parameters such as p^H, contact time, adsorbate concentration, and adsorbent dosage. The optimum conditions for maximum adsorption capacity were determined at p^H=3, adsorbent dosage = 300 mg and contact time = 90 min. Langmuir and Freundlich isotherms were employed in order to evaluate optimum adsorption capacity. The maximum adsorption capacity was obtained by Langmuir isotherm is of 10.124 mg/g. The Legergren kinetics of adsorption studies of Cr (VI) followed Pseudo second order.

Index Terms: Chromium IV, tamarindus indica, p^H, Isotherms, Kinetics.

1 INTRODUCTION

Chromium exists usually in both trivalent and hexavalent forms in aqueous solutions. Cr (III) is relatively insoluble and required by microorganisms in small quantities as an essential trace metal nutrient, while Cr (VI) is a great concern because of its toxicity. Cr (VI) has been reported to be a primary contaminant to animals, plants and microorganisms and known to be carcinogenic [1]. Sources of chromium waste leading to water pollution includes electroplating, steel fabrication, paints and pigments, mining, leather tanning, textile dyeing, aluminum conversion coating operations, plants producing industrial inorganic chemicals and wood treatment units. Due to environmental concern, discharge limits of both Cr (III) and Cr (VI) have been instituted by most industrial countries. Their concentration in industrial wastewater ranges from 0.5 to 270,000 ppm [2]. The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1 ppm and in potable water is 0.05 ppm. In general Chromium (VI) can be removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction and evaporation. Among these methods adsorption is the most efficient technique because of its convenience, easy operation and simplicity of design and effective for the removal of Cr (VI) from aqueous solutions and industrial effluents. In the present study, tamarind seeds are used as a low-cost adsorbent for the removal of Cr (VI) from aqueous solutions.

2 MATERIALS AND METHODS

2.1 PREPARATION OF ADSORBENT

Potassium dichromate was used for the preparation of stock Cr (VI) solution in double distilled water. Adjustment of p^H during the experiment was done by using hydrochloric acid and sodium hydroxide solutions. Concentrated sulfuric acid (98% w/w) was used for the treatment of tamarindus indica seeds collected from local market Bahir Dar, Ethiopia. The seeds were washed with double distilled water and dried for three days and then powdered by using crusher. The powder was sieved in 10-12 mesh size. Tamarindus indica powder was treated with concentrated sulfuric acid (98% W/W) in 1:1 weight ratio. The treated powder was washed with distilled water, NaOH to make p^H to 7 and the treated powder was dried for 4 hours and, then soaked in 1% $NaHCO_3$ solution for 3 days and then dried.

2.2 PREPARATION OF ADSORBATE

A stock solution of 1000 ppm of Cr (VI) solution was prepared by dissolving 2.8287 g of Potassium dichromate in one liter double distilled water.

2.3 BATCH ADSORPTION STUDIES

The adsorption experiments were carried out at room temperature, i.e., 30±2 ^{0}C using batch technique to obtain both the rate and equilibrium data. The experiments were conducted by varying contact time, pH, adsorbent dosage, adsorbate concentration. The batch experiments were carried out in a 100 ml of conical flask. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time. The contents of the flask were filtered through filter paper. The equilibrium concentration of Chromium VI in the solution was determined by reacting with 1,5- diphenyl carbazide and the adsorption was measured in a UV - visible spectrophotometer at 479 nm.

The amount of Cr (VI) adsorbed per unit mass of the adsorbent was evaluated by using the following mass balance equation,

$$q = \frac{C_i - C_e}{W} \times V \qquad (2.1)$$

Where V is the volume of the solution (L) and W is the amount of adsorbent (g); C_i and C_e (mg/L) are the initial and equilibrium metal concentrations respectively.

The percent removal of Cr (VI) was calculated as follows.

$$\%\text{Removal of Cr (VI)} = \frac{C_i - C_e}{C_i} \times 100 \qquad (2.2)$$

3 RESULTS AND DISCUSSION

3.1 Effect of Contact Time:

Chromium VI adsorption was studied using adsorbent dosage of 5g/L and hexavalent Chromium concentration of 5 mg/L. The experiments were carried out to study the effect of contact time ranging from 10 to 150 minutes. The effect of contact time on adsorption is shown in the Fig.1. Experiments show that the time of contact has influence on the percentage removal of Cr (VI). The percentage removal of Cr (VI) from aqueous solution increases rapidly and reaches a value of 80.2 % at 10 min. The adsorption process becomes slower in the later stages and reaches to maximum of 99% at 90 min; further increase in time has no effect on the % removal of Cr (VI).

3.2 Effect of Adsorbent Dose:

The adsorption capacities for different doses were (100 mg to 600 mg) studied by keeping all other parameters constant. The effect of adsorbent dose on the % removal of Chromium (VI) is reported in the Fig.2. It is observed that, the % removal of Cr (VI) increases with Adsorbent Dose. The maximum % removal was observed at 300 mg and further increase in dosage has no effect on removal of Cr (VI) by keeping all other parameters constant.

3.3 Effect of P^H:

P^H is an important factor in the adsorption process. The effect of P^H on the adsorption efficiency of Tamarind tree seeds in the P^H range 3 – 11 was studied at different initial concentrations of Cr (VI) and the same is shown in the Fig.3.The P^H of the system controls the adsorption capacity due to its influence on the surface properties of the adsorbent and ionic forms of chromium solutions. The maximum % removal of Cr (VI) was 99 from a solution 5 mg/L at P^H 3. The adsorption of Cr (VI) was decreased very rapidly by increasing either P^H or concentration of Cr (VI).

3.4 Effect of Initial Chromium (VI) Concentration:

The adsorption of Cr (VI) was studied by varying PH (3, 5 and 9) and Cr (VI) Concentration (5, 10, 20, 30, 40 and50 mg/L) keeping constant 5 g/L of adsorbent dose and contact time 90 minutes. The results were plotted in Fig.4. The percentage removal of Cr (VI) increases with decrease in adsorbate concentration and P^H. This is due to, at the lower concentrations there are sufficient active sites that the adsorbate can easily occupy.

3.5 Adsorption Isotherms:

Adsorption studies were conducted at fixed amount of adsorbent dose by varying initial concentration of Cr (VI) in the solution. The equilibrium data was verified with Langmuir, Freundlich and Temkin adsorption isotherms as shown in the Fig.5, Fig.6 and Fig.7 respectively. The Langmuir Isotherm is given by

$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L q_0 C} \qquad (3.1)$$

Where,

q = the amount of metal adsorbed per gram of the adsorbent, mg/g

C = the equilibrium concentration of adsorbate, mg/L

q_0 = maximum monolayer coverage capacity, mg/g

K_L = Langmuir isotherm constant, L/mg

The above equation describes quantitatively the formation of monolayer adsorbate on outer surface of the adsorbent.

The Freundlich isotherm is as follows

$$\log(q) = \log(K_F) + \frac{1}{n}\log(C) \qquad (3.2)$$

Where,
q= The amount of metal adsorbed per gram of the adsorbent, mg/g
K_F= Freundlich isotherm constant, mg/g
C = the equilibrium concentration of adsorbate, mg/L
n=Adsorption intensity

The Temkin linearised Adsorption isotherm is given by

$$q = \frac{RT}{b_T}\ln(A_T) + \frac{RT}{b_T}\ln(C) \qquad (3.3)$$

Where,
A_T=Temkin Isotherm Equilibrium binding constant, L/g
b_T= Temkin Isotherm constant,
R=Universal Gas Constant, J/mole-K
T=Absolute temperature, K
Table 1 describes the parameter coefficients of adsorption isotherms.

3.6 Kinetics Study:

The adsorption of Cr (VI) on treated tamarind seeds powder was investigated and the chemical reaction kinetics may be described by Legergren models as pseduo first order and pseudo second order which are expressed as follows

$$\frac{dq}{dt} = k_1(q_e - q) \qquad (3.4)$$

Where q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium, mg/g
q= the amount of metal adsorbed per gram of the adsorbent at any given time‘t’, mg/g
k_1 is the pseudo first order rate constant, min^{-1}.

By using the boundary conditions and simplifying the above equation becomes

$$\ln(q_e - q) = \ln q_e - k_1 t \qquad (3.5)$$

The pseudo second order reaction model is expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \qquad (3.6)$$

On integration of above expression with boundary conditions, the linearized form is

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3.7)$$

The experimental data is fitted to the above equations as shwon in Fig.8 and Fig.9. The Legergren Pseudo first order and Second Order model correlation coefficients were calculated and are given in the Table 2. The correlation coefficients were in good agreement with Pseudo second order kinetics.

4 CONCLUSION

Tamarindus Indica seeds used to study the removal of Chromium VI from aqueous solutions by adsorption process. Various Experimental studies were conducted by different parameters like p^H, contact time, adsorbate concentration, and adsorbent dosage. The optimum conditions for maximum removal were obtained at p^H=3, adsorbent dosage = 300 mg and contact time = 90 min. Langmuir and Freundlich isotherms were employed in order to evaluate optimum adsorption capacity. The maximum adsorption capacity was obtained by Langmuir isotherm is of 10.124 mg/g. The Legergren kinetics of adsorption studies of Cr (VI) followed Pseudo second order.

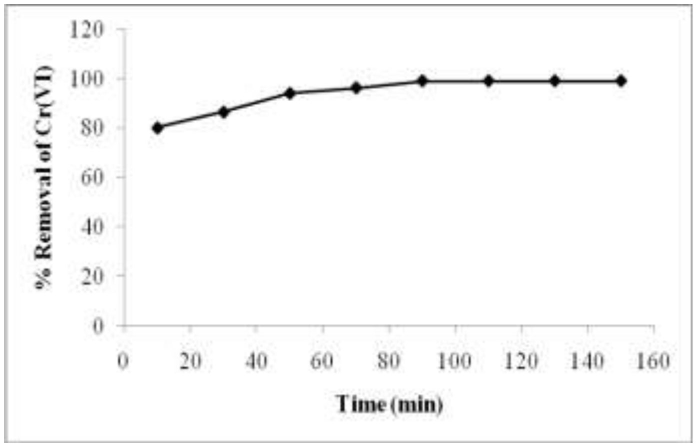

Figure 1. Effect of Contact time on Cr (VI) removal

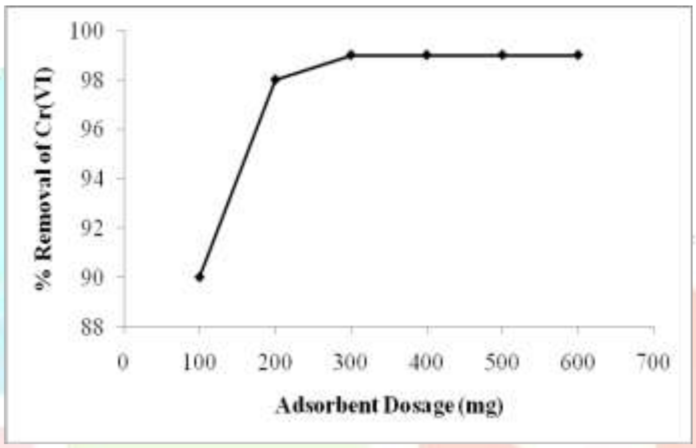

Figure 2. Effect of Adsorbent Dose on % removal of Cr (VI)

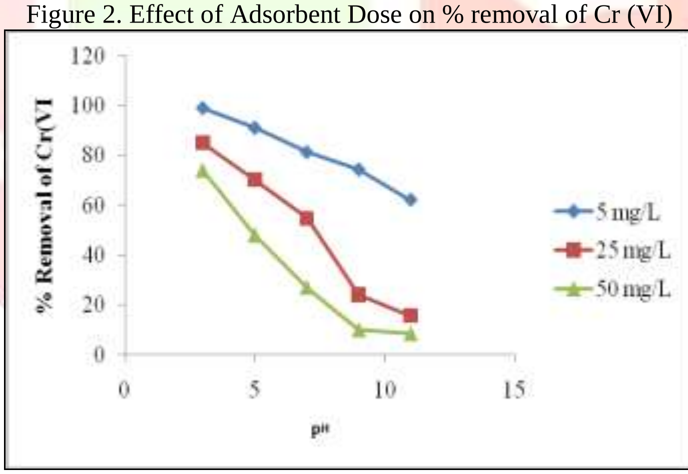

Figure 3. Effect of P^H on % removal of Cr (VI) at initial Chromium (VI) concentration = 5, 25, 50 mg/L and Adsorbent Dose 5g/L.

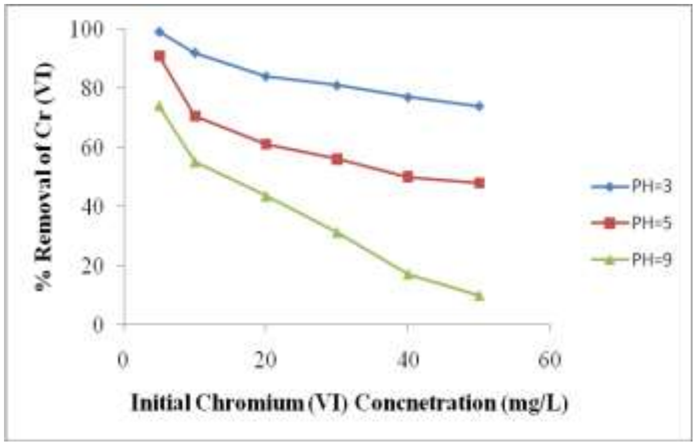

Figure 4. Effect of Adsorbent initial concentration on % removal of Cr (VI) at different P^H = 3, 5 and 9.

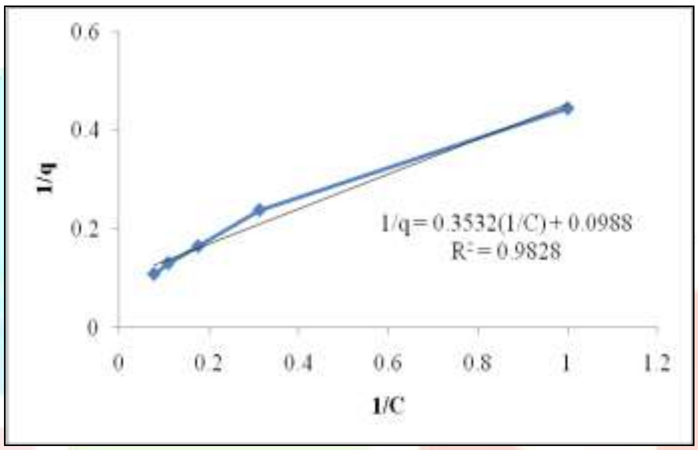

Figure 5. Langmuir Adsorption Isotherm

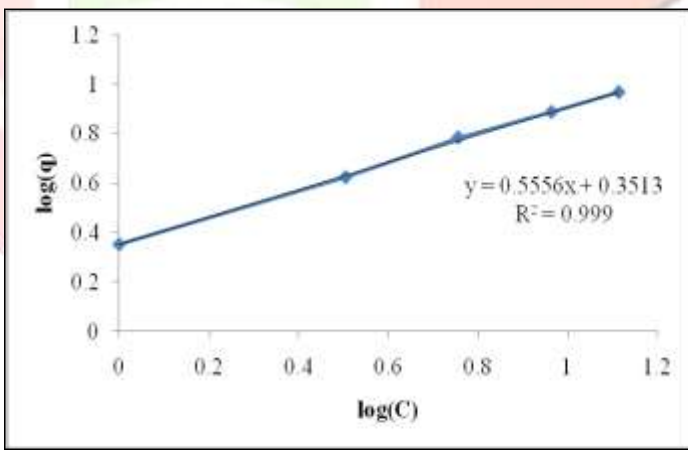

Figure 6. Freundlich Adsorption Isotherm

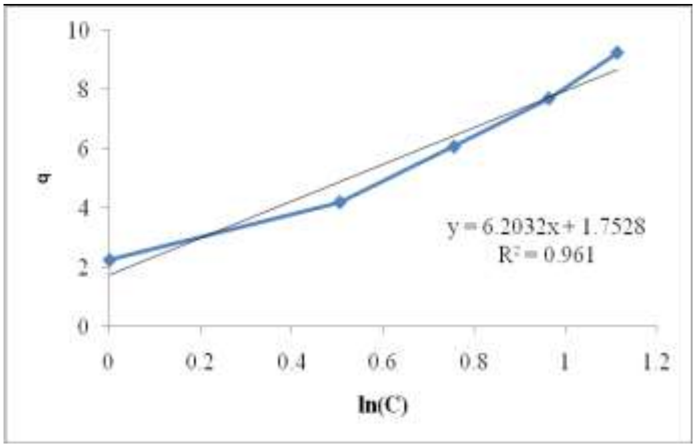

Figure 7: Temkin Adsorption Isotherm Studies

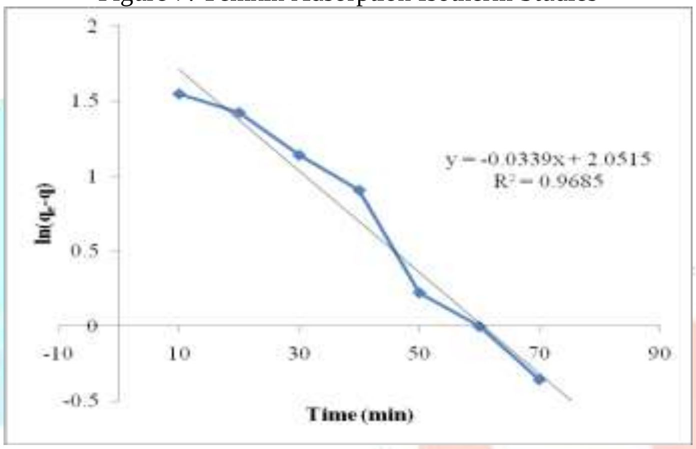

Figure.8 Pseudo First Order Reaction Kinetics plot for adsorption of Cr(VI)

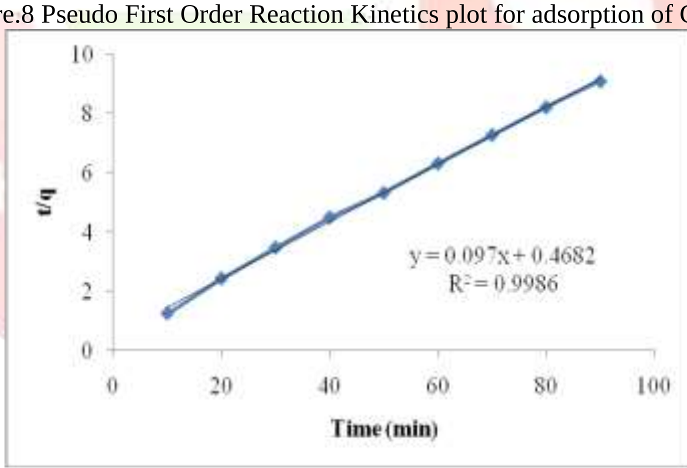

Figure.9 Pseudo Second Order Reaction Kinetics plot for adsorption of Cr(VI)

Table 1. Parameters of Isotherm Models for Cr (VI) Adsoprtion using Tamrind Seeds

Isotherms	**Parameters**		
Langmuir	q_0 (mg/g) 10.124	K_L (L/mg) 0.2797	R^2 0.9828
Freundlich	K_F (mg/g)(L/g)n 1.799	n 2.245	R^2 0.999
Temkin	b_T (J/mol) 406.1	A_T (L/g) 1.326	R^2 0.961

Table 2. Correlation Coefficients of Kinetic Studies

Parameters	Pseudo First Order Kinetics	Pseduo Second Order Kinetics
Rate Constant	k_1=0.0339 min^{-1}	k_2=0.02 g/g.min
Capacity, q_e (mg/g)	7.779	10.31
R^2	0.9685	0.9986

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