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Sustainable Chemisorption: Removal Of Direct Orange Dye From Aqueous Solutions By Adsorption Onto Waste Corn Cob

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Abstract

Corn cob waste was investigated as a low -cost and effective adsorbent for the adsorption of Direct Orange dye from aqueous solution. Physico-Chemical characteristics of the adsorbent were studied as per the standard testing methods. Effect of various parameters such as agitation time, adsorbent dose and concentration, pH, temperature have been investigated in the present study. The adsorption of dyes have been best described by pseudo second order kinetic model and Langmuir and Freundlich adsorption Isotherms. The negative values of the ΔG^o and positive value of the ΔH^o indicate that the sorption process is spontaneous and endothermic in nature. The positive value of ΔS^o shows the increasing randomness during adsorption process. Desorptive studies reveals that no satisfactory desorption taking place indicating chemisorptive nature of adsorption.

Key Words

Corn cob waste, Direct Orange, Adsorption Isotherm,Kinetics, Desorption

Introduction

Pollution caused by the textile wastewater is a common problem faced by many countries. Dyes used in the textile industry are particularly difficult to remove by the conventional waste treatment methods because of their stability towards light and oxidizing agents and resistance toward aerobic digestion. A number of advanced wastewater treatment schemes have been proposed for water quality enhancement. Most of these treatment methods use a combination of biological,chemical and physical processes. The activated carbon adsorption treatment has been proven to be an effective replacement for the combined biological and chemical treatment although at a relatively high cost. The need of low cost replacements for activated carbon initialized a number of studies.

In this study an attempt has been made to explore the possibility of using food crop waste such as corncob. Globally corncob is one of the major causes of solid waste.Corn cob waste is an effective and sustainable adsorbent for removing pollutants from water and other liquids due to its porous structure and high cellulose content[1]. It can be used in its natural form or activated to enhance its adsorption capacity for a variety of substances including heavy metals,dyes and emulsified oil[2]. Corn cob waste is a renewable, biodegradable and low-cost agricultural byproduct making it an environmentally friendly choice[3].Utilizing this waste material increases its economic value and supports a circular economy approach.

Materials and Methods

Preparation of the adsorbent (Corn cob)

Corn cob samples collected were air-dried at room temperature were crushed, ground and sieved to particle size less than 0.25µg.The obtained powders washed thoroughly using deionized water,dried in the oven at 100°C till constant weight and washed using hydrochloric acid toeliminates impurities and make the corn cob in chloride form.Samples rewashed using deionized water and dried in the oven at 100°C[4,5]. The high cellulose, hemicellulose and lignin content provides active sites for adsorption.

Adsorbate

Dye was purchased from Loba chemicals. Stock dye solutions of 1000mg/L were prepared by dissolving an appropriate quantity of dyes.Working solutions at appropriate concentrations were prepared by diluting the stock solution. Distilled water was used throughout the experiments.

Characterization studies

Physico- chemical characteristics of the adsorbent were studied as per the standard testing methods [6]. The surface area of the adsorbent was determined by usual method..Presence of some functional groups were identified by FTIR analysis. Functional groups like O-H stretching indicating the presence of hydroxyl groups from water and polysaccharides (3600 – 3200 cm^{-1}), C-H stretching from hydrocarbon structures (2900 – 2800 cm^{-1} and 1400 – 1300 cm^{-1}) and C=O stretching from carbonyl and carboxylic on surface are particularly important for binding. The surface morphology of the adsorbent was visualized via Scanning Electron Microscopy (Fig.1).

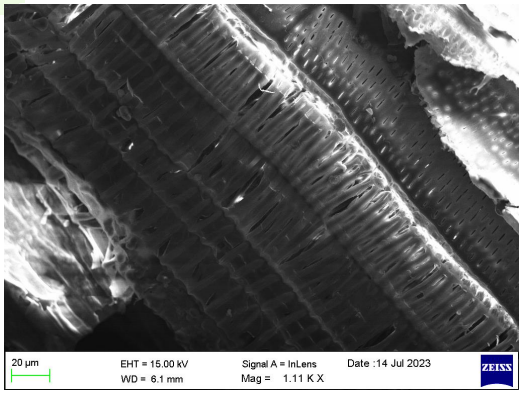

Figure 1. FESEM analysis of adsorbent

Batch Adsorption Studies

Adsorption experiments were conducted using the batch method at temperatures of 302 K, 307 K, 312 K, 317 K, and 322 K. A known weight of the adsorbent was introduced into 50 mL of dye solution with initial concentrations ranging from 10 to 40 mg/L. The contents were thoroughly shaken using a mechanical shaker operating at 120 rpm for 100 minutes. The unadsorbed supernatent liquid was analyzed for residual dye concentration using a UV-Visible Spectrometer (JASCO V750). The pH of the adsorptive solution was adjusted using 0.1 N NaOH and 0.1 N HCl, measured with a Deluxe pH Meter (Model 101E). All experiments were conducted in duplicate, and the mean values of the two measurements were used for calculations.

Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent. Desorption studies as a function of pH were conducted to analyze the possibility of reuse the adsorbent for further adsorption and to make the process more economical. After adsorption experiments the dye loaded adsorbent was washed gently with double distilled water to remove any un-adsorbed dye if present. Desorption studies were conducted using several such samples.500mg of the dye loaded adsorbent agitated above the equilibration time with 50ml of double distilled water of various pH.

Results and Discussion

Adsorption of Direct Orange using Corn cob

i. Effect of Initial Dye Concentration and Agitation Time

The effect of agitation time and initial concentration on sorption at pH is depicted in Fig 2. The percent sorption exhibited a increasing trend as the agitation time increased and reached an equilibrium state at 100 minutes is found sufficient and also invariant for equilibrium for various initial concentrations of dye 10,20,30,40 mg/l. The sorption capacity of activated carbon of cotton stalks is found to be greater than those of other activated carbon obtained from other materials[7].

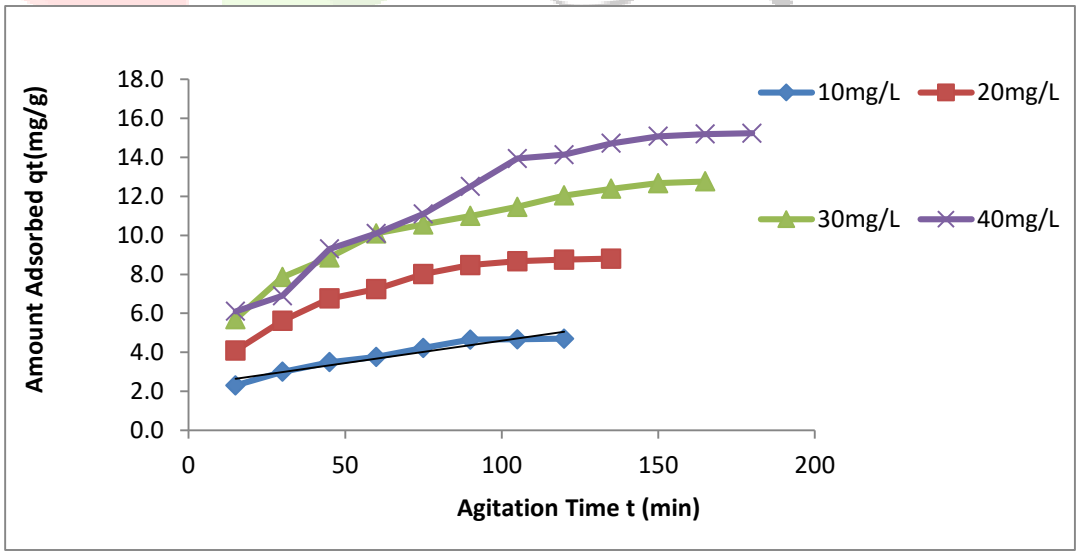

Figure 2 Influence of Concentration

Conditions: Adsorbent dose: 100mg/50ml; Initial pH: 6.0; Temp.: 302 K

ii. **Effect of Sorbent dosage**

The effect of sorbent dosage on dye uptake was investigated (Fig.3) and the rate of sorption increases with increase in dose of adsorbent.This is due to the increase in active sites for adsorption of dye molecules with increasing sorbent dosage.The sorption equilibria of the dye were reached at 125 mg/l and the removal of dyes remained almost invariable above this dosage.Therefore 125 mg/l appears to be the optimum sorbent dosage for the studied conditions.

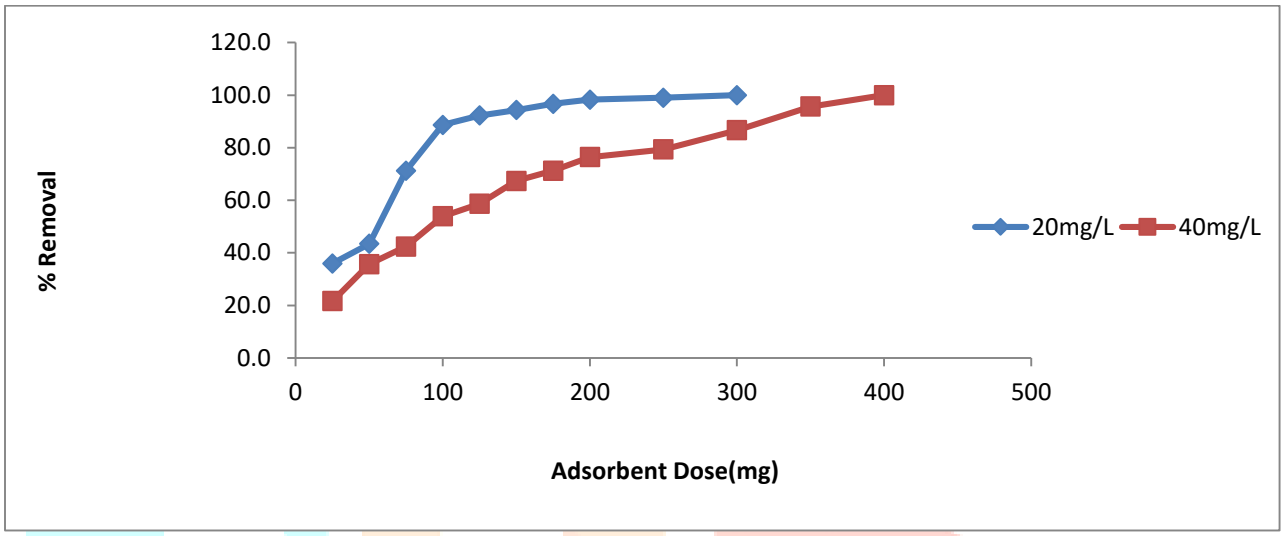

Figure 3 influence of adsorbent dosages

Conditions: Agitation time: 3 hrs; Initial pH: 6.0; Temp.: 302 K

iii. Effect of pH

The pH factor is very important in the adsorption process especially for dye adsorption. The effect of pH on the adsorption of Direct Orange with corn cob was studied.It was observed that the pH has a significant influence to the adsorption process (Fig.4). Figure 4 shows that the maximum uptake of Direct Orange dye was observed at pH 10 (91 %).At pH between range 3 to 7, the removal was increased from 50% to 84 %. As the pH value increased from 7 to 10, the efficiency of the dye removal is slightly becoming lesser. The low adsorption of Direct Orange at acidic pH was suggested to be due to the presence of excess H^+ ions in solution. Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption,while for anionic dyes the percentage of dye removal will increases[7].For cationic dyes.the lower adsorption of dye at acidic pH is probably due to the presence of excess H+ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the pH solution, the electrostatic repulsion between the positively charged cationic dye and the surface of adsorbent is lowered consequently the removal efficiency is increased.

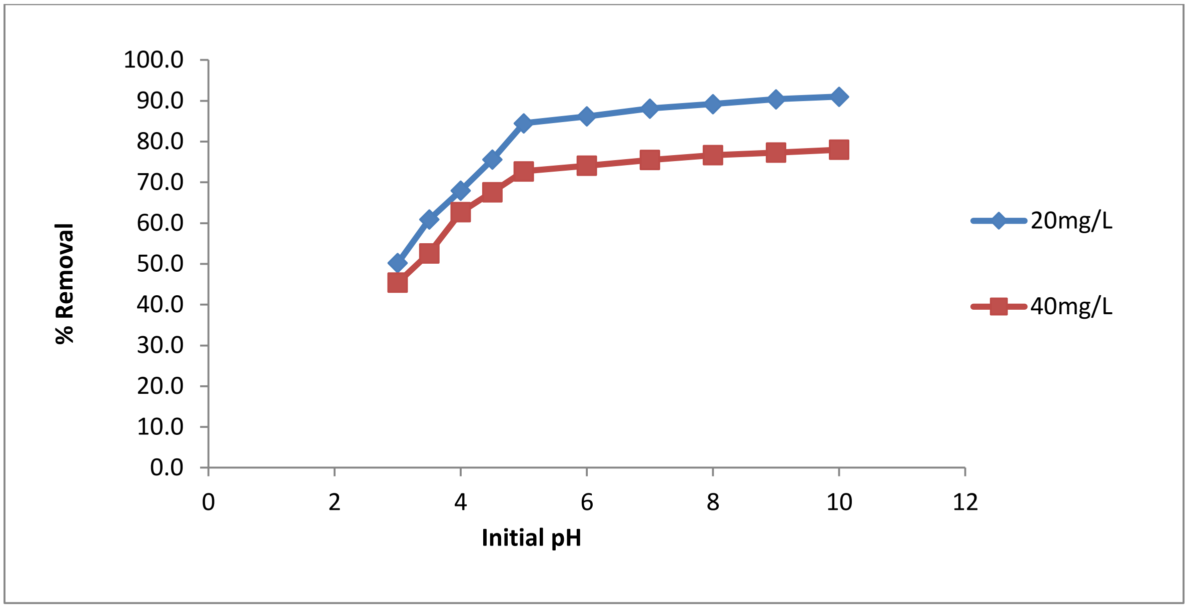

Figure 4 Influence of initial pH of dye solution

Conditions: Agitation time: 3 hrs; Adsorbent dose: 100mg/50ml; Temp.: 302 K

iv. Sorption Kinetics

The kinetics and dynamics of adsorption of Direct Orange on Corn cob have been studied by applying the First order , Second order and Elovich kinetic models (Fig. 8,9).

1. Pseudo first order equation

The kinetics of sorption process follows first order rate expression of Lagergren equation (1)

$Log(q_e – q) – log\ q_e = k_1 t/2.303$ ……………………. (1)

Where q_e and q (both in mg/g) are the amounts of dye adsorbed at equilibrium and at time t, respectively, and $k_1$is the adsorption rate constant.The plots of $Log(q_e – q)$ versus time t at different temperatures and at different initial concentrations of dye. In this study the experimental data does not fit well with the pseudo first order order equation(1) for the whole range of contact time.

2. Pseudo second order equation :

The adsorption may also be described by pseudo second order kinetic model. The linearised form of the pseudo second order model is

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad \text{……………………………………………. (2)}$$

k_2 –rate constant of second order adsorption (g/mg/min)

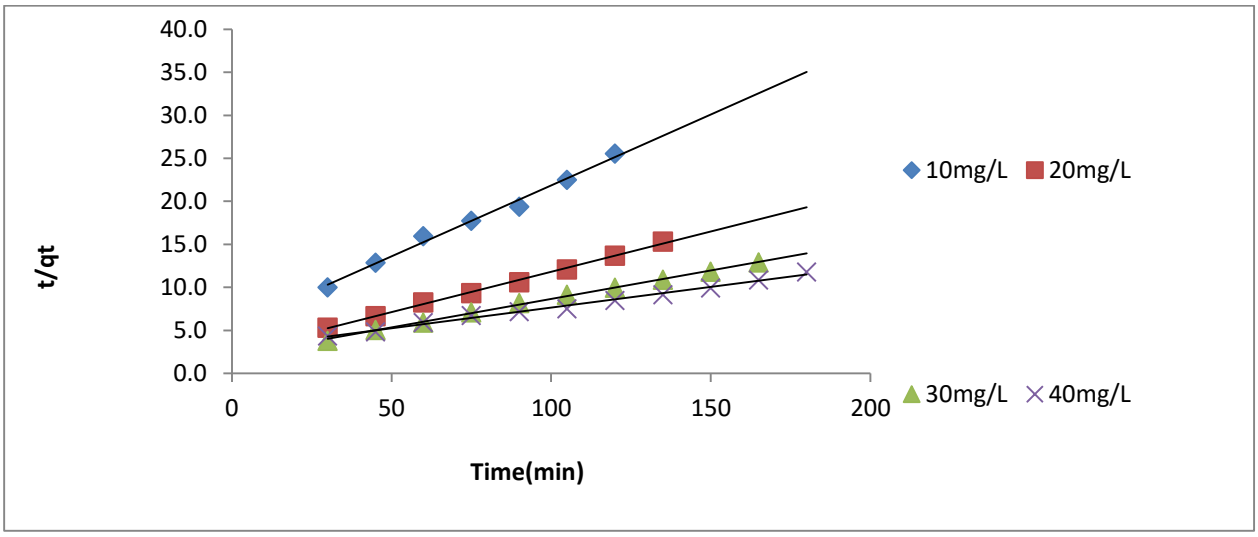

Figure 5. Pseudo second order Kinetic Model

From the results (Fig.5) it can be suggested that pseudo second order kinetics[7] describes the adsorption of Basic violet 14 by fruit waste much better than pseudo first order kinetic model.

3. **Elovich equation:**

The Elovich equation is mainly applicable for chemisorption kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as

$$dq_t/dt = a \exp(-bq_t) \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

a,b are constants

a – initial adsorption rate (mg/g/min)

b – extent of surface coverage and activation energy for adsorption (g/mg)

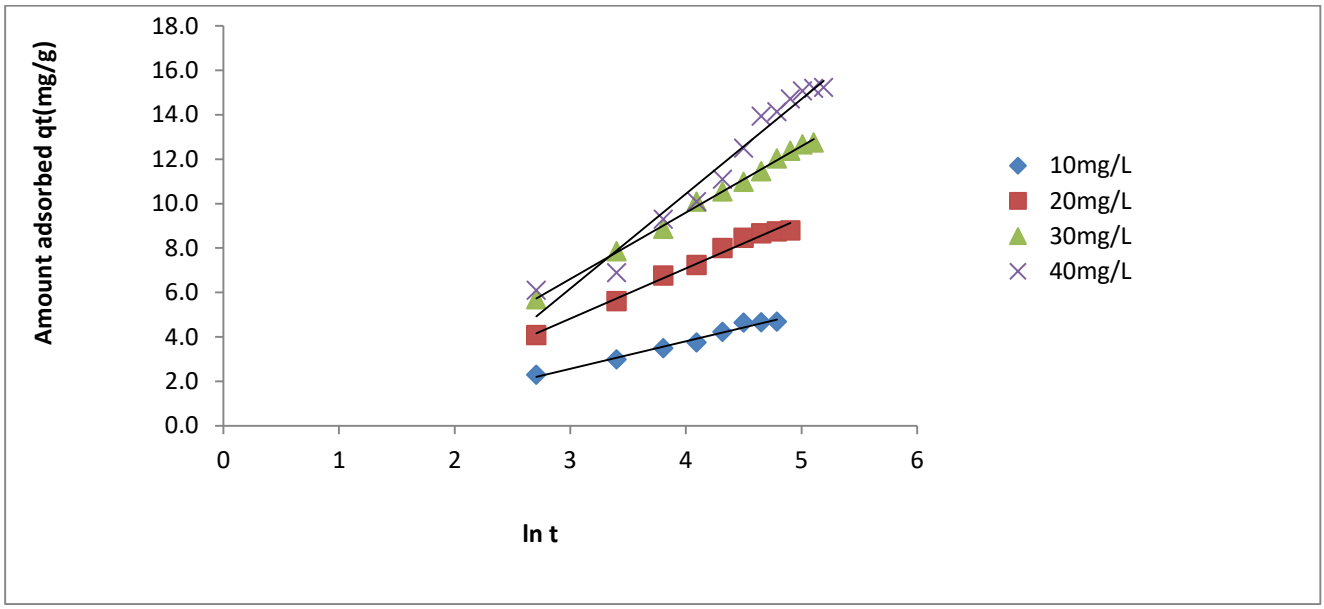

Figure 6, Elovich Model

The plot of q_t versus ln t gives a linear trasce with good correlation coefficient. The results shows that adsorption follows pseudo second order kinetics and Elovich kinetic model very well.

v. Sorption Isotherm

The adsorption data were analysed with the help of the following linearised forms of Freundlich and Langmuir isotherms .

Freundlich isotherm : $\log q_e = \log K + 1/n \log c_e$ …….. (4)

Langmuir isotherm : $c_e/q_e = 1/Q_o b + c_e/Q_o$ …….. (5)

Where

K= adsorption capacity

(1/n) = order/intensity of adsorption

q_e = amount of dye adsorption per unit mass of adsorbent (mglg)

c_e = equilibrium concentration of dye (ppm)

Q_o = monolayer (maximum) adsorption capacity (mglg)

b = Langmuir constant related to energy of adsorption (l/mg)

The values of Freundlich and Langmuir[7] parameters have been obtained respectively,from the linear correlation between the values of (i) log q_e and log c_e and (ii) (c_e / q_e) and c_e (Fig. 7 a and b).

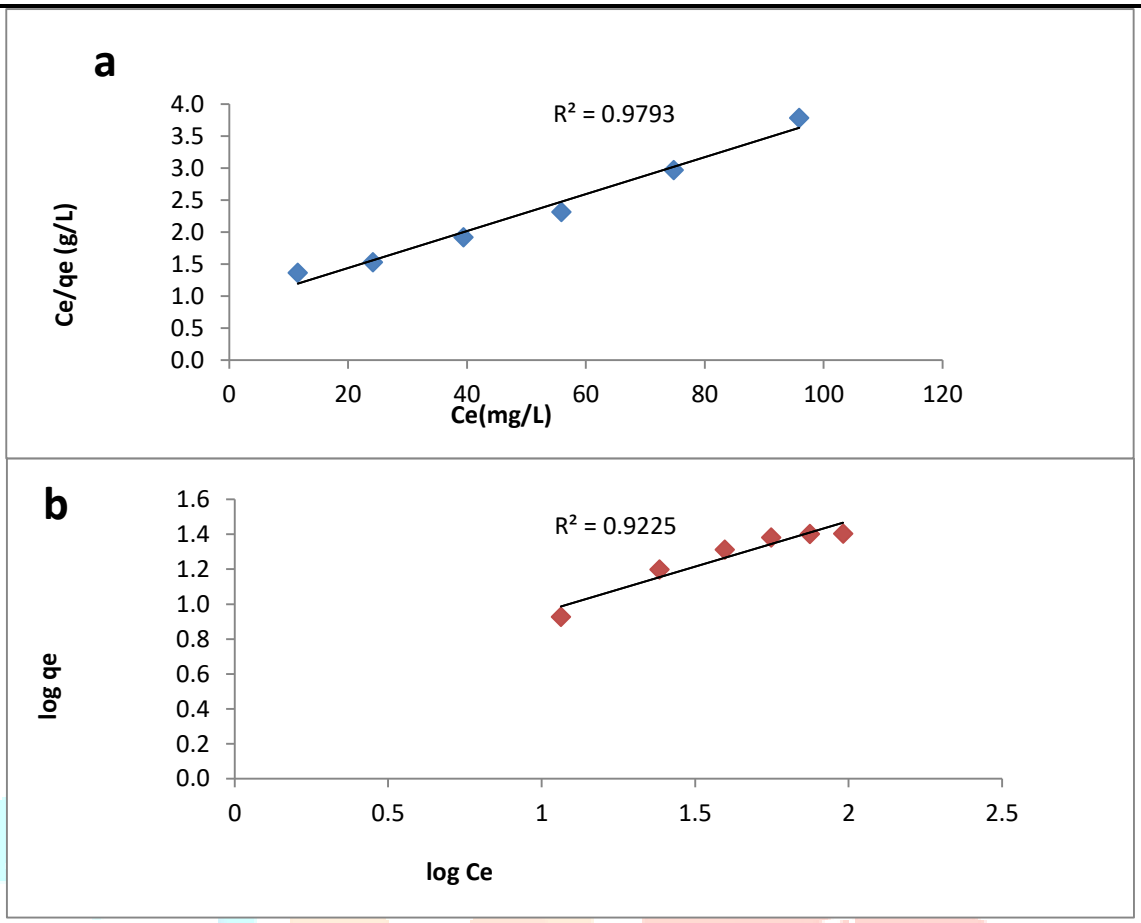

Figure 7. Sorption isotherms a) Langmuir Plot b) Freundlich Plot

vi. **Effect of Temperature**

Increase of temperature hardly increased q_e value. The thermodynamic parameters was determined using the following equations.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad \text{..... (6)}$$

$$\Delta G^\circ = -RT \ln Kc \quad \text{..... (7)}$$

The negative value of Gibbs free energy change (ΔG°) indicates the spontaneous nature of adsorption[7]. The results are shown in Fig.8 (Table - 1)

Table 1 Effect of Temperature

Dye	-ΔG° K J /mol			K_c			ΔS° J / K / mol	ΔH° KJ / mol
	302 K	312 K	322 K	302 K	312 K	322 K		
Direct Orange	12.89	14.25	15.61	0.716	0.827	0.897	46.14	16.81

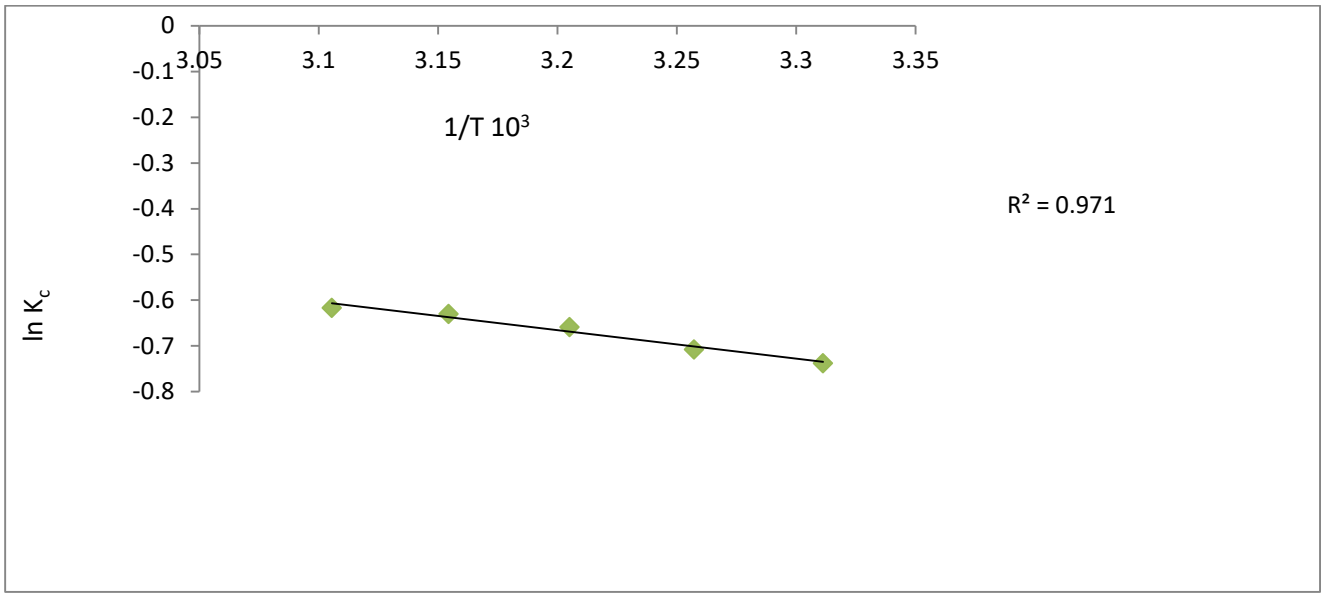

Figure 8 . Eyrings plot

vii. **Intra Particle Diffusion Study**

The possibility of intra particle diffusion process was explored by using the Weber and Morris intra particle diffusion model is,

$$q_t = k_i t^{0.5} + C \quad \text{..... (8)}$$

where

q_t - Amount of dye adsorbed at time t (mg/g)

C - intercept

k_i - intra particle diffusion rate constant (mg/g/min$^{-1/2}$)

The value of C gives an insight into the thickness of the boundary layer. Large intercept suggests great boundary layer effect. Similar results were reported in literature[8].

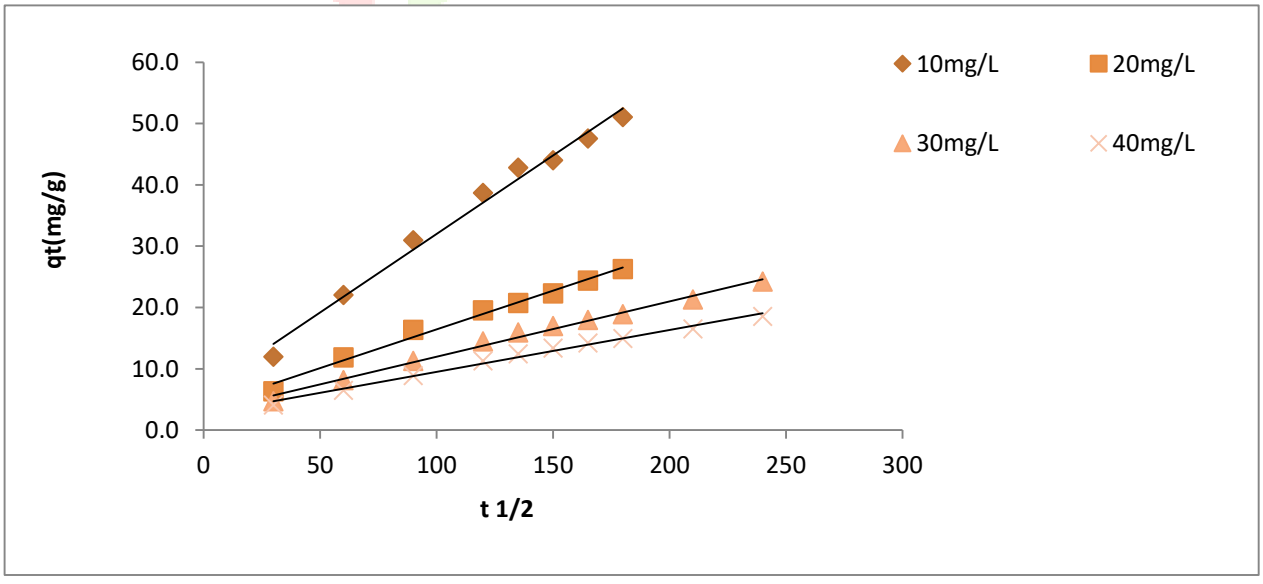

Figure 9. Intra Particle Diffusion Model

b. Desorption studies

To test the reversibility of the adsorbed dye molecules,desorption experiments were done using water ,dil.HCl and dil.AcOH as the desorbing agents[9].For this dye loaded adsorbent particles,after filtration,were kept in contact with 50ml of desorbing solutions for 4 hours and concentrations of dyes extracted was determined. Among these acetic acid was found to be better desorbing agent,it may be concluded that the dye must be attached to the adsorbent through an interaction of chemisorptions type.

2. Conclusion

The present study reveals that adsorbent (Corn cob) can be used as an ideal sorbent for effective removal of dye (Direct Orange) from industrial wastewater because it has rod-shaped morphology with amorphous nature.The extent of sorption being dependent on sorbent dosage, temperature and also on the initial concentration of dye. Moreover, the phenomenon of sorption of dye is pH dependent and the optimum pH range from 3 to 7. The phenomenon of sorption is endothermic and the rate of sorption is more than 94%. Since corn cob are abundantly available, inexpensive and non-toxic wastes, its adsorption as an adsorbent for dye removal seems to be viable and economical.

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