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Phosphoric Acid Activated Cotton Stalks (Gossypium Hirsutuml) As Low Cost Adsorbent For The Removal Of Direct Orange: Equilibrium And Kinetic Studies

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Abstract: Cotton Stalks (Gossypium Hirsutum L) waste was investigated as a low-cost and effective adsorbent for the adsorption of Direct Orange from aqueous solution. The effects of initial dye concentration, contact time, pH effect, adsorbent dosage and temperature on the adsorption parameters wereinvestigated. The Langmuir and Freundlich adsorption models were evaluated using experimental data. The maximum adsorption capacity was found to be from the Langmuir model. The dimensionless separation factor (RL) values lies between 0.0576and0.1548, indicated favourable adsorption. The adsorption rate data were analyzed according to the Lagergren pseudo first, second order model, Elovich and intraparticle diffusion models. The negative values of the ΔG°at 302-322K and the positive value of the ΔH° (KJ/mol) indicate the adsorption process is spontaneous and endothermic in nature. The positive value of ΔS° J/mol/K) shows the increasing randomness during adsorption process. Desorption studies suggest that the adsorption of Direct Orange dye onto Cotton Stalks involves chemisorption.

***Index Terms* - ** Direct Orange, Cotton Stalks, Adsorption Isotherms, Sorption mechanism.

I. INTRODUCTION

Textile industries discharged large quantity of highly coloured wastewater effluent which are released into nearby land or rivers without any treatment because the conventional treatment methods are very expensive.1On the other hand the low cost technologies don't allow a wishful colour removal and have certain disadvantages. Thus the colour from effluent is one of the major environmental problem. The methods of colour removal from industrial effluents include biological treatment, coagulation, floatation, adsorption, oxidation and hyper filtration. Among the treatment options, adsorption appears to have considerable potential for the removal of colour from industrial effluents. As adsorption onto activated carbons is a well known process for micro pollutants removal2. It has many advantages over several other conventional treatment methods for wastewater treatment. These include (i) less land area (ii) lower sensitivity to diurinal variation (iii) not getting affected by toxic chemicals (iv) greater flexibility in the design and operation and (v) superior removal of organic contaminants3. Activated carbon is perhaps the most widely used adsorbent for the removal of many organic contaminants which are biologically resistant, but activated carbon is prohibitively expensive. The technology to manufacture activated carbon of good quality is not fully developed in developing countries. Moreover, there are many problems connected with the regeneration used activated carbon. Therefore, there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale. Cotton Stalks an agro waste, which is available in large quantities at no cost and can form a good basis for the development of adsorbent materials. A number of studies, however, have so far been focused on the use of cotton stalks for the removal of dyes from wastewater4-6.In this work, cotton stalks, low cost and agro based waste after harvest of cotton crops readily available in plenty were chemically activated and used for the removal of the Direct Orange dye.

II. MATERIALS AND METHODS

Materials

Preparation of the adsorbent

The adsorbent used in the present study is cotton stalks were collected and boiled with phosphoric acid in 1 : 3 ratio for half an hour, cooled and washed several times with water to remove excess phosphoric acid and dried at 383K for 12 hours in a hot air oven and sieved into particle size of 0.200 – 0.300 mm.

Preparation of adsorbate

The basic dye Direct Orange was used as an adsorbate in the present study. A stock solution of 1000 mg/L was prepared in double-distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions.

Methods

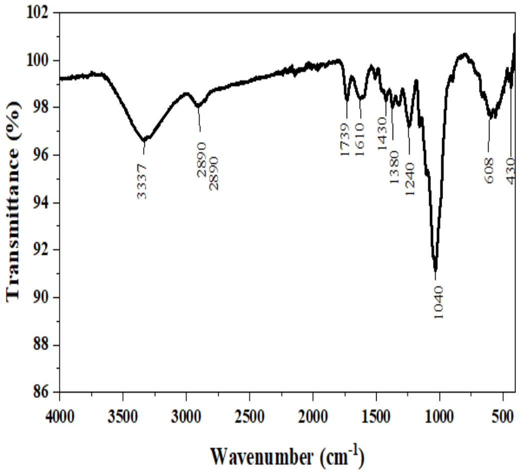
Characterization analysis of the adsorbent material

The physico-chemical characteristics of treated cotton stalks were studied as per the standard testing methods7and reported in Table-1. Presence of some functional groups were identified by FTIR analysis(Fig. 1).The surface morphology of the adsorbent was visualized via Scanning Electron Microscopy (Fig.2).

Table 1 Characteristics of Adsorbent

S. No.	Parameter	Value
1.	Bulk Density G/Ml	0.89
2.	Specific Gravity	0.36
3.	Porosity %	69.26
4.	Moisture	12.86
5.	Ash %	3.10
6.	Volatile Matter %	11
7.	Solubility In Water %	0.55
8.	Solubility In 0.25M Hcl %	3.10
9.	Ph_{zpc}	6.12
10.	Decolourising Power	25.78
11.	Iodine Number Mg/G	322.62
12.	Surface Area M^2/G	252
13.	**Functional Groups**	

	Carboxyl Groupmeq/G	0.189
	Phenolic Groupmeq/G	0.828
	Lactonic Groupmeq/G	0.053



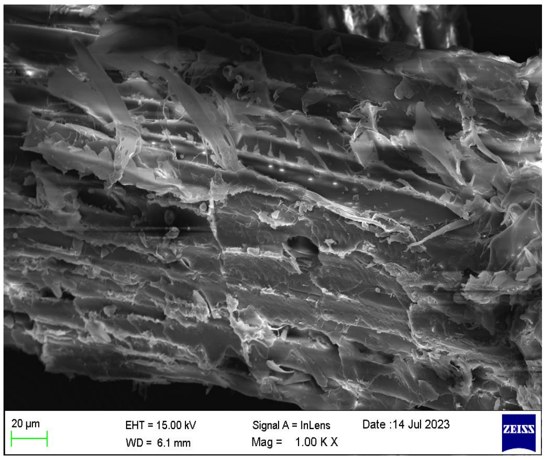


Fig. 1 **Fig. 2**

Adsorption Studies

Batch adsorption experiments were carried outat room temperature (29°C). Exactly 50 ml of Direct Orange dye solution of known concentration(10-40 mg/L) was shaken at the constant agitation speed (200rpm) with a required dose of adsorbents for a specific period of contact time(5-180 min) in a mechanical shaker, after noting down the initial pH of the solution to the optimum pH. The pH of the solutions were adjusted to the required value by adding either 0.1N HCl or 0.1N NaOHsolution. After equilibrium the final concentration (Ce) were measured. The percentage removal of dye were calculated using the following relationship:

% Removal of dye = $C_i - C_e/C_i \times 100$

Where Ci and Ce are the initial and final (equilibrium) concentrations of dye (mg/L) respectively. Blanks containing no dye were used for each series of experiments as control.

III. RESULTS AND DISCUSSION

i) Effect of Initial Dye Concentration and Agitation Time

Effect of agitation time on the amount of dyes adsorbed per unit time of adsorbent was investigated for Direct Orange, the equilibrium reached at 120,160,180 and 220 min for an increase in initial dye concentrations of 10,20,30 and 40 mg/L with a fixed concentration of 100mg/50ml at room temperature respectively, removal degree decreases from 80.5 % to 49.1 %.(Fig.3). It can be explained with the fact that with increase in dye concentration in solution, the quantity of active sites decreases on the adsorbent surfaces and therefore sorption degree decreases. Similar results have been reported in literature.

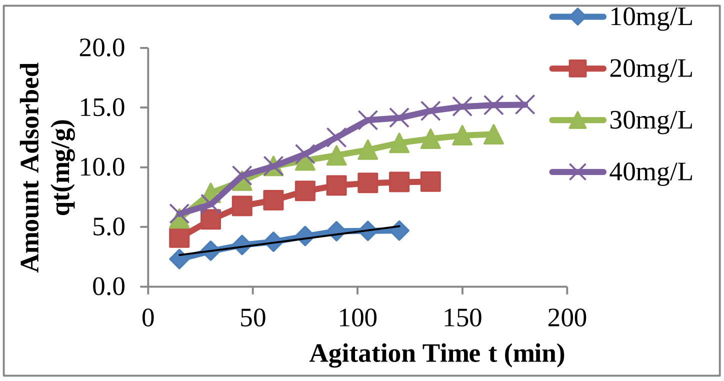


Fig.3 Effect of Agitation time and Initial dye concentration

ii) Effect of Sorbent dosage

The effect of sorbent dosage on dye uptake was investigated by varying the amount of cotton stalks from 100mg/L to 700 mg/L. The effect of sorbent dosage on the removal degree of dye is shown in Table-2. The percentage removal of Direct Orange increased with the increase of dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose conglomeration of the adsorbent.

Table 2 Effect of Adsorbent Dose

Adsorbent Dose (mg)	**% Removal**	
	20 mg/L	**40 mg/L**
100	26.89	24.66
150	32.78	30.87
200	37.21	34.12
250	41.76	37.67
300	43.98	39.89
350	57.43	45.34
400	63.78	56.87
450	78.34	62.43
500	83.97	75.79
550	88.64	81.46
600	90.21	85.12
650	94.32	89.23
700	98.67	92.76

iii) Effect of pH

The effect of pH on the adsorption of Direct Orange with cotton stalks was studied. It was observed that the pH has a significant influence to the adsorption process. Figure shows that the maximum uptake of Direct Orange dye was observed at pH 8 (78.8%).The results are shown in Fig.4.

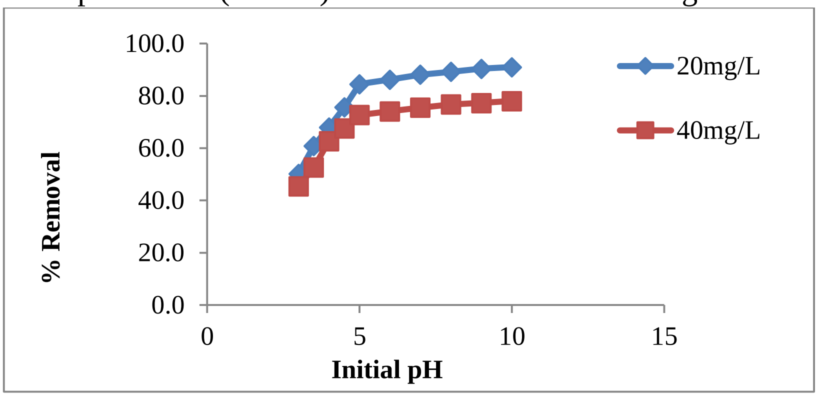


Fig. 4 Effect of pH

Effect of Temperature

Temperature has important effects on the adsorption process. As the temperature increase, rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent particle increases. Table - 3 shows effect of different temperature for Direct Orange dye removal on treated cotton stalks adsorbent. The amount of Direct Orange dye adsorbed increase with increasing temperature from 302K to 322K, indicating the adsorption process is endothermic.

Table 3 Effect of Temperature

Temperature (Kelvin)	% Removal
302	38.41
307	49.23
312	63.06
317	72.48
322	90 5

Adsorption Isotherm

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

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

Langmuir isotherm : $c_e/q_e = 1/Q_o b + c_e/Q_o$ ……………………………. (2)

Where

K= adsorption capacity

(1/n) = order/intensity of adsorption

q_e = amount of dye adsorption per unit mass of adsorbent (mg /g)

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[12,13] and Langmuir[14,15] 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. 10 a and b).

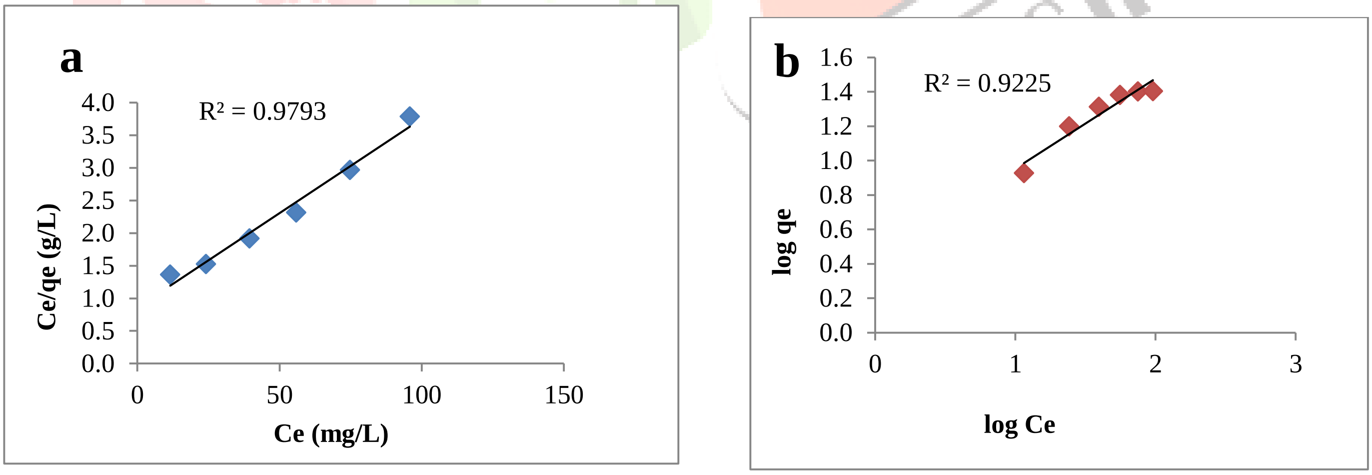


Fig.5. Adsorption isotherms a) Langmuir Plot b) Freundlich Plot

Adsorption Kinetics

The kinetics and dynamics of adsorption of Basic violet 14 on Cotton Stalks have been studied by applying the First order 8, Second order 9 and Elovich kinetic10,11 models (Fig. 6,7).

Pseudo first order equation

The kinetics of sorption process follows first order rate expression of Lagergren equation (3)

$\text{Log}(q_e - q) - \log q_e = k_1 t/2.303$ …………………… (3)

Where $q_e$andq (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 $\text{Log}(q_e - q)$ 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 equation(1) for the whole range of contact time.

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

$t/q_t = 1/k_2 q_e^2 + t/q_e$

…………………… (4)

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

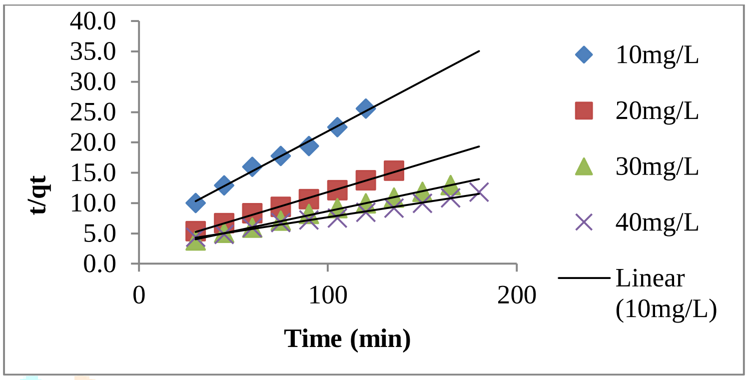


Figure 6 Pseudo second order Kinetic Model

From the results (Fig.6) it can be suggested that pseudo second order kinetics describes the adsorption of Basic violet 14 by fruit waste much better than pseudo first order kinetic model.

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

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

…………………. (5)

a,b are constants

a – initial adsorption rate(mg/g/min)

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

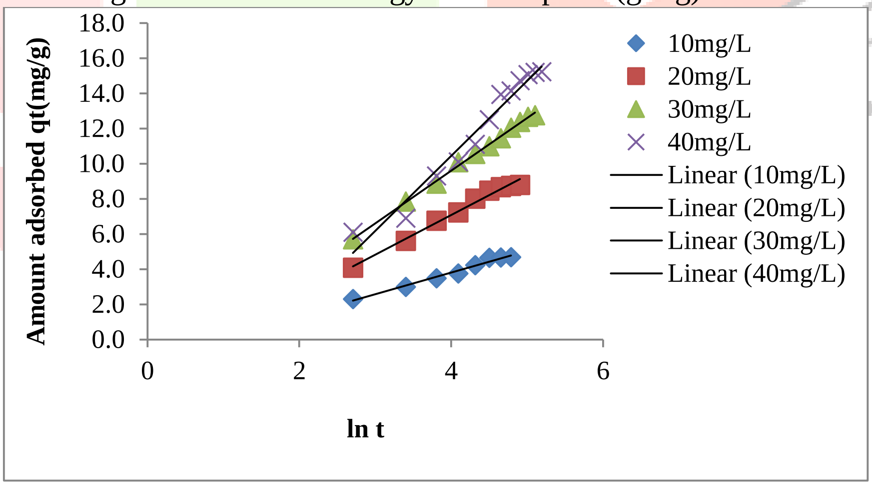


Figure 7 Elovich Model

Intra Particle Diffusion Study

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

$q_t = k_i t^{0.5} + C$

…………………………… (6)

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[18,19].

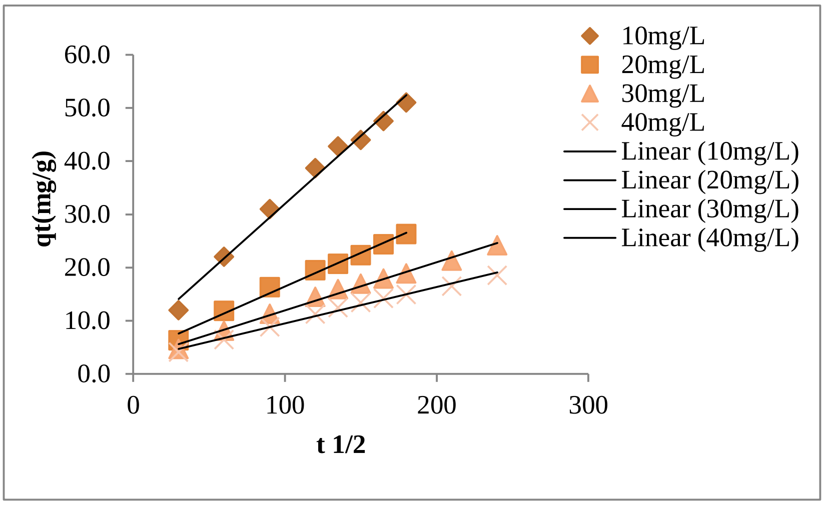


Figure 8 Intra Particle Diffusion Model

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[20, 21]. 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.

IV. CONCLUSION

The present investigation showed, the efficiency of treated cotton stalks as adsorbent for the removal of Direct Orange dye from aqueous solutions was investigated. Batch mode adsorption studies indicate that the adsorption process was strongly dependent on initial dye concentration, adsorbrnt dose, contact time, pH and temperature. The equilibrium sorption data obtained at different initial concentrations of dye fitted well in the Langmuir and Freundlich isotherm models. Kinetic studies show that the dye removal followed pseudo second order rate equation, while thermodynamic studies suggest that the sorption process was spontaneous and endothermic in nature. The positive value of $\Delta S°$ shows the increasing randomness during adsorption process. The offered mechanism of adsorptive process of the Direct Orange dye on a surface of the adsorbent, obtained on the basis of cotton stalks, considers forming a complex between dye and adsorbent. It is finally concluded that treated cotton stalks, common and easily available agro-waste material, can be used as a adsorbent for the removal of Direct Orange dye from aqueous solutions.

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