



## Removal of the Dye Chromotrope 2R Using Activated Carbon Prepared from *Salvadora persica*: Kinetic and Equilibrium Studies

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### ABSTRACT

The study was aimed at investigating the use of activated carbon prepared from *Salvadora persica* (ACSP) and the results were compared with the polyvinyl alcohol coated carbon prepared from *Salvadora persica* (PVAC-SP). Various factors affecting the adsorption process including solution pH, contact time, adsorbent dose and initial dye concentration were studied in a batch process. PVAC-SP was found to be most effective at pH 8. The kinetics of adsorption process was well described by the pseudo 2<sup>nd</sup> order kinetics model. The maximum adsorption of dye with ACSP and PVAC-SP were found to be 71.3% and 92.7% respectively.

### INTRODUCTION

The pollution of water due to various types of synthetic dyes has been a major cause of concern since long. The dye bearing wastewater discharged into water contributes negatively and upset aquatic life. The discharge from the textile industries is solution of complex chemicals (Alafano 1983). The colour is due to unfixed dye. Nature of dyes and dying process affect the concentration of unused dye. It is unfit for recycling without proper treatment. Adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Therefore, one of the powerful treatment processes for the removal of dyes from water with a low cost is adsorption. The adsorption on naturally occurring plant waste as chemically activated carbon was studied for removal of dye from its aqueous solution on a laboratory scale. The adsorption efficiency depends on the particle size. There are many methods to activate the charcoal to increase its surface area. The adsorption of the dye Chromotrope 2R on both ACSP and PVAC-SP was found to confirm the two isotherms. The adsorption data fit well with the Langmuir and Freundlich isotherm models. In this paper the comparative studies to explore the potential of activated carbon (ACSP) and poly vinyl alcohol coated carbon (PVAC-SP) to treat dyes have been conducted. The objective of the work was preparation and adsorption capacities of activated carbon prepared from leaves of *Salvadora persica*, a desert plant and poly vinyl alcohol coated carbon.

### MATERIALS AND METHODS

**Preparation of polyvinyl alcohol coated carbon of *Salvadora persica* (PVAC-SP):** The naturally dried leaves of the plant *Salvadora persica* were obtained locally and cut into small pieces. The leaves were treated with sulphuric acid (2% v/v) in 1:1 ratio and were kept in an oven at 150°C for 24 hours. The residue was filtered and washed with distilled water repeatedly to remove sulphuric acid (washings tested with two drops of barium chloride solution) and finally dried. Chemical activation using sulphuric acid produces a high surface area and high degree of microporosity.

Polyvinyl alcohol is a good hydrophilic polymer and has water-adsorbing capacity. The powdered ACSP was treated with an emulsion of readily available synthetic polymer-PVAC. Nine parts by weight of activated carbon obtained from the leaves of *Salvadora persica* (ACSP) was mixed with one part by weight of PVAC to form a semisolid mass. The agglomerated product was dried and ground into fine powder. The adsorbent was sieved to 40-60-mesh size and dried at 110°C for 2 hours. This powder was then used as an adsorbing material.

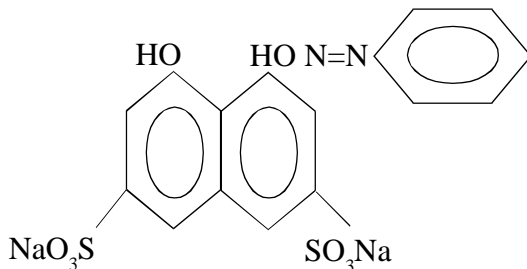


Fig. 1: Structure of the dye Chromotrope 2R.

## RESULTS AND DISCUSSION

**Adsorption studies:** Adsorption studies were carried out by batch adsorption process at room temperature. Synthetic samples containing the required amount of the dye Chromotrope 2R were prepared by dissolving the desired amount of the dye in double distilled water. In the adsorption measurement dye solutions at different concentrations (50, 70, 90, 110, 130 and 150 ppm) and pH of 3, 5, 8, 10 and 12 were used. The initial pH of the solution was adjusted by using 0.1 M sodium hydroxide and/or 0.1 M nitric acid, without changing the volume of the sample. The equilibrium adsorption of dye was reached after 80 min (Fig. 1). The solutions were stirred at constant speed. The suspension was then allowed to settle, supernatant solution was decanted and analysed on UV-VIS spectrophotometer for concentration of dye between time intervals 20-130 min. The removal efficiency ( $E$ ) of the adsorbent was defined as:

$$E (\%) = [(C_0 - C_e) / C_0] \times 100$$

Where,  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of dye solution (mg/L), respectively.

The increase in initial dye concentration increases the amount of dye uptake per unit weight of the ACSP and PVAC-SP (Fig. 2). The maximum adsorption capacities found were as follows: 7.13 mg dye/g ACSP and 9.27 mg dye/g PVAC- SP for 50 ppm solution. By comparing the results of the present study, it can be concluded that the adsorption efficiency of PVAC-SP is greater than ACSP for the adsorption of dye from aqueous solution.

**Adsorption isotherm models for dye:** The Langmuir adsorption isotherm and the Freundlich isotherm are two common isotherms used to describe equilibria.

Freundlich equation has the following general form.

$$(X/m) \text{ or } q_e = K_f C_e^{1/n}$$

The linearised Freundlich adsorption isotherm has the form:

$$\text{Log } q_e = \text{log } K_f + 1/n \text{ Log } C_e$$

Where,

$q_e$  = the amount of the adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent)

$X$  = the amount of the adsorbate

$m$  = mass of adsorbent used (g)

$K_f$  = adsorption capacity

$n$  = adsorption intensity (the empirical constants)

$C_e$  = equilibrium concentration of adsorbate (mg/L)

The equilibrium concentration was calculated using the following formula:

$$C_e = C_0 - (\% \text{ adsorption} \times C_0 / 100) \quad C_0 = \text{initial concentration of adsorbate (mg/L)}$$

The amount of the adsorbate adsorbed per unit mass of adsorbent  $q_e$  (mg adsorbate/g adsorbent) was evaluated by the following formula:

$$q_e = (C_0 - C_e) \times V / m \times 1000$$

Linear plots of  $\log q_e$  (x/m) vs.  $\log C_e$  at different adsorbent doses are applied to confirm the applicability of Freundlich models as shown in Fig. 3.

Langmuir isotherm has the following general form.

$$C_e / q_e = 1 / Q_m b + C_e / Q_m$$

$Q_m$  and  $b$  is Langmuir constants related to adsorption capacity (maximum specific uptake corresponding to the site saturation) and energy (intensity) of adsorption (l of adsorbent/mg of adsorbate) respectively. The Langmuir isotherm plot between  $C_e / q_e$  and  $C_e$  is given in Fig. 4. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter  $R_L$  that defined as (Weber & Chakraborty 1974).

$$R_L = 1 / (1 + bC_0)$$

Where,  $C_0$  (mg/L) is the initial concentration of the dye.

Values of dimensionless equilibrium parameter  $R_L$  show the adsorption to be favourable ( $0 < R_L < 1$ ).

The values of Langmuir and Freundlich constants calculated from the graph are summarized in Table 1 for the dye by PVAC-SP and ACSP. Value of  $n$  for dye at effective dose and contact time, indicates good adsorption potential of the adsorbent. Values of  $R_L$  and  $R^2$  show the adsorption to be more favourable.

### Adsorption Kinetics

$$t / q_t = 1 / h_0 + 1 / (q_e) t$$

Where,

$h_0$  = the initial adsorption rate (mg/g min)

$q_e$  = the amount of dye adsorbed at equilibrium (mg/g)

$q_t$  = the adsorbed at time  $t$  (mg/g)

The initial adsorption rate,  $h_0$ , at  $t = 0$  is defined as:

$$h = K_2 q_e$$

Where,  $K_2$  is the pseudo second order rate constant for the adsorption process (g/mg min).

Table 1: Values of Freundlich and Langmuir constants for adsorption of Chromotrope 2R on PVAC-SP and ACSP at 80 min. and at optimal dose of 5g/L.

Adsorbent	Freundlich Constants				Langmuir constant			
	$K_f$	1/n	n	$R^2$	Qm(mg/mg)	b (1/mg)	$R_L$	$R^2$
ACSP	0.1498	0.5895	1.6963	0.9978	20.36	0.0251	0.2844	0.9982
PVAC-SP	0.5828	0.3744	2.6709	0.9976	26.5957	0.1201	0.0768	0.9927

R = Correlation coefficient

Table 2: Pseudo second order parameters for ACSP and PVAC-SP at pH 8.

Parameters	ACSP			PVAC-SP		
	50ppm	70ppm	90ppm	50ppm	70ppm	90ppm
$K_2$	$2.94 \times 10^{-3}$	$2.5 \times 10^{-3}$	$2.9 \times 10^{-3}$	$8.5 \times 10^{-3}$	$7.4 \times 10^{-3}$	$6.8 \times 10^{-3}$
$R^2$	0.9832	0.9879	0.9919	0.997	0.9984	0.9989
$Q_e$	9.59	11.90	12.77	10.30	13.47	16.36
h	0.2713	0.3615	0.4733	0.9121	1.3581	1.8402

Table: 3 Intra-particle diffusion rate constants for Chromotrope 2R.

Adsorbent	Linear equation	$K_{id}$	a	$R^2$
ACSP	$Y = 0.3992x + 0.0535$	1.131	0.3992	0.9635
PVAC-SP	$Y = 0.1647x + 0.6363$	4.328	0.1647	0.9434

The initial adsorption rate  $h_0$ , the equilibrium adsorption capacity, and the pseudo second order rate constant  $K_2$ , were determined from the slope and intercept of the plot of  $t/q_t$  against  $t$  (Table 2).

Based on linear regression ( $R^2$ ) values, the kinetics of dye adsorption onto ACSP and PVAC-SP for 50 ppm solution can be described well by pseudo second order ( $R^2 = 0.9832$  and  $R^2 = 0.997$ ) equation. The pseudo 2nd order kinetic model plot for the dye by ACSP and PVAC-SP at optimum conditions are shown in Fig. 5. The results clearly indicate that this model fit progressively well with increasing adsorbate concentration.

### Intra-Particle Diffusion

The most commonly used technique for identifying the mechanism involved in the adsorption process is by using intra-particle diffusion model expressed as (Igwe & Abia 2005):

$$q = K_{id} (t)a$$

A linearised form of the equation is given as:

$$\log q = \log K_{id} + a \log (t)$$

Where,  $q$  is the fraction of the amount adsorbed, 'a' is the gradient of linear plots,  $t$  is the contact time (min), and  $K_{id}$  is the intra-particle diffusion rate constant ( $\text{min}^{-1}$ ).

The intra-particle diffusion plot for the dye by ACSP and PVAC-SP are shown in Fig. 6. The regression equations and R values for intra-particle diffusion model is shown in Table 3 for ACSP and PVAC-SP at optimal dose 5 g/L. The values of 'a' and  $K_{id}$  were calculated from the slopes and

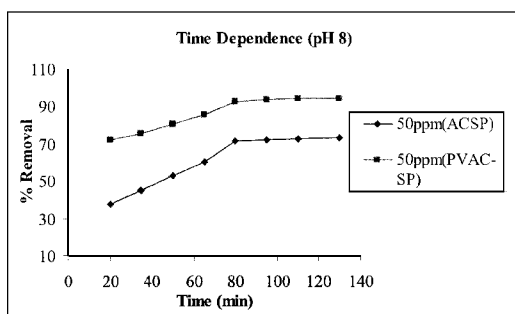


Fig. 1: Effect of contact time on removal of chromotrope 2R at different concentrations by ACSP and PVAC-SP at pH8.

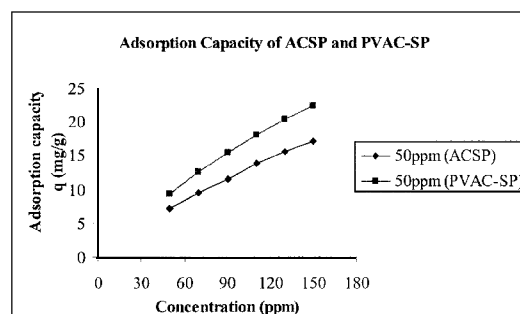


Fig. 2: Effect of initial concentration of chromotrope 2R on adsorption capacity of ACSP and PVAC-SP at equilibrium contact time 80 min and at effective pH 8.

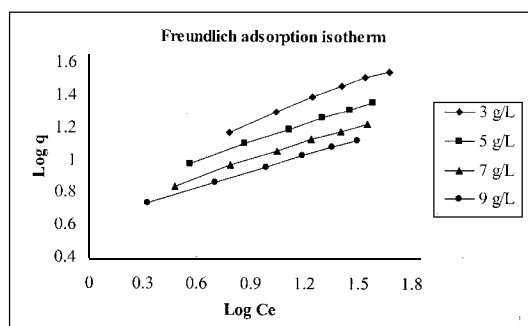


Fig. 3: Freundlich isotherm plot of chromotrope 2R adsorption by PVAC-SP at optimum conditions.

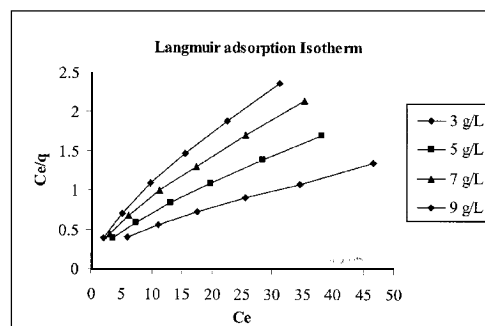


Fig. 4: Langmuir isotherm plot for chromotrope 2R adsorption by PVAC-SP at optimum conditions.

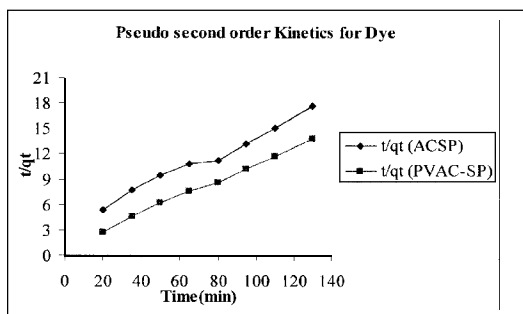


Fig. 5: Pseudo 2<sup>nd</sup> order kinetic model plot for chromotrope 2R by ACSP and PVAC-SP at optimum conditions.

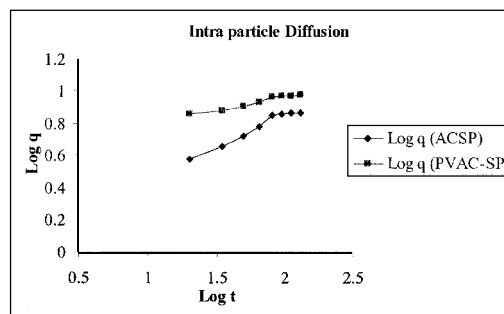


Fig. 6: Intra-particle diffusion plot of chromotrope 2R by ACSP and PVAC-SP at optimum conditions.

intercepts of the plot respectively. The values of 'a' depicts the adsorption mechanism and  $K_{id}$  may be taken as a rate factor. Higher values of  $K_{id}$  illustrate an enhancement in the rate of adsorption.

### CONCLUSION

According to the results, it can be concluded that PVA coated adsorbent is more effective in the removal of dye at low pH values and concentration. *Salvadora persica* which is available in

abundance locally is the most efficient adsorbent and much cheaper than activated carbon. The adsorbed amount of Chromotrope 2R dye on PVAC-SP and its adsorption rate are higher than ACSP.

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