



Dye Removal of Adsorption Study in Thespesia Populnea Seed

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ABSTRACT

The potential of Thespesia Populnea Seed (TPS) powder, for the removal of Congo red 4B (CR) dye from aqueous solution was investigated. The adsorbent was characterized by FTIR and SEM analysis. Batch adsorption studies were conducted and various parameters such as pH, adsorbent dosage, initial dye concentration, contact time and temperature were studied to observe their effects in the dye adsorption process. The optimum conditions for the adsorption of Congo red 4B onto the adsorbent TPS was found to be contact time 75 min^{-1} , pH 3, temperature 303K for an initial dye concentration 22 mg/L and adsorbent dosage 0.12gm. The experimental equilibrium adsorption data fitted to the Langmuir isotherm and Freundlich isotherm model. The kinetic data conformed to the Pseudo second order kinetic model, suggesting that the rate limiting steps may be chemisorptions. Thermodynamic quantities such as Gibbs free energy ΔG^0 , enthalpy ΔH^0 and entropy ΔS^0 were evaluated. The negative values of ΔG^0 and the negative value of ΔH^0 obtained indicated the spontaneous and exothermic nature of the adsorption processes while the negative ΔS^0 value obtained decreased randomness during the adsorption process.

Keywords: Adsorption, Thespesia Populnea seed, Congo red 4B

INTRODUCTION

Adsorption technique is by far the most versatile and widely used moreover, this processes become

economic if the adsorbent used is available and cheap in cost. Thespesia Populnea (Malvaceae) is a large tree found in tropical regions and coastal forests of India opine¹. Various parts of T. Populnea are found to possess useful medicinal properties, such as antibacterial, antioxidant, purgative, anti fertility, anti-inflammatory and heap to protective active opine². Moreover, all the parts of the TPS plant have been used in traditional system of medicine. Industries manufacturing dye and dye intermediates are the largest sector of chemical industries in India. There is a variety of dyes like acid dyes, basic dyes, azo dyes, mordant dyes, plastic dyes, etc. The effluents from these industries thus contain dyes as main pollutant³⁻⁶. Dye contaminated waste water originates from various industries such as textile, leather, food, dyeing, cosmetics etc. consequently, there is a considerable need for the removal of dye from water effluents prior to their discharge in to receiving water⁷. A huge amount of water us necessary by these industries for the cleaning and washing purpose and they discharge highly colored effluents containing different dyes. Many investigators have studied the feasibility of inexpensive alternative material like pear millet husk, date pits, sawdust, buffing dust of leather industry, coir pith, crude oil residue tropical grass, olive stone and almond shells, pines bark, wood waste, coconut shell, etc., as carbonaceous precursors, for the removal of dyes from water and waste water. Present study Congo red 4B is one of the types of acid dyes. Congo red 4B is a heterocyclic aromatic chemical compound with molecular formula

$C_{32}N_{22}N_6Na_2O_6S_2$ fig. 1 Shows the structure of Congo red 4B, its chemical name is sodium salt of Benzidine azo-bis-naphthylamine-4 sulfonic acid and molecular weight is 696.66 g/mol. Due to color change from blue to red at pH 3-5 can be used as pH indicator.

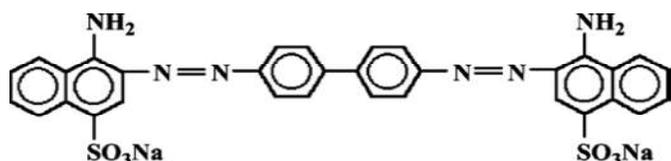


Fig. 1 Structure of Congo red 4B dye

In the presence of color in the water bodies reduce light penetration which in turn upsets the biological metabolism process, disposal of dye waste water without proper treatment destructed the aquatic communities present in the ecosystem and some dyes are reported to cause allergic dermatitis, skin irritation, cancer and mutation in humans if they are discharged as wastewater without any treatment⁸⁻¹². There are no reports in this plant for adsorption studies. This prompted us to do research work in this adsorption of Congo red 4B dye using biomass from *Thespesia Populnea* seed.

MATERIAL AND METHODS

MATERIAL

Thespesia Populnea seed (TPS) Ennore, Congo red 4B dye Cas.No: ASC 2562 Kevin laboratory (Avara synthesis Pvt.Ltd.), pH meter, UV-1800 Double Beam Spectrophotometer-(Shimadzu), FTIR- Fourier transform spectrophotometer, SEM-Scanning electron microscopy (TEQIP Equipment), Orbital shaker, R-BC Laboratory centrifuge and Weighing machine and Air oven (Shimadzu).

METHODS

Adsorbent Collection and Preparations (TPS): The *Thespesia Populnea* Seed (TPS) was collected from Ennore (India). Their seed was washed thoroughly with running tap water to removed sand, dirt and other impurities present in it and dried in sunlight for one week until all moisture were remove dried in an oven at 50°C. It was the ground well in a mixer and sieved powdered. The TPS powder that passed through the sieve were stored in an air tight container labeled TPS and used as adsorbent without any further treatment.

Preparation of Adsorbate Solution: Analytical grade Congo red 4B dye ($C_{32}N_{22}N_6Na_2O_6S_2$) Molecular weight 696.68g/mol $\lambda_{max}=495nm$ was obtained from the UV-spectrophotometer (Shimadzu UV-1800) from Anna University (EM laboratory). Purchased Avara synthesis Pvt.Ltd. Low cost adsorbent. A stock solution Congo red 4B dye of concentration 100 mg/L was prepared by dissolving of 0.1g of powder adsorbate dye in 1L standard flask filled with distilled water. Experimental dye solution of desired concentration was obtained by appropriate dilution of the stock solution. Correlation coefficient value of dye concentration 100 mg/L value ($R^2=0.997$).

Batch Adsorption Experiments

Batch adsorption of Congo red 4B dye onto the adsorbent TPS was conducted in a 250ml conical flask containing 40ml of known concentration of the CR dye solution and accurately weighed amount of the adsorbents. The mixtures in the flask were agitated on a mechanical shaker at a constant speed of 250 rpm. The effect of contact time (30, 45, 60 and 75) min⁻¹, Adsorbent dosage (0.08, 0.10, 0.12 and 0.14) gm, Initial dye concentration (22, 24, 26, 28 and 30) mg/L, pH (3, 4, 5, 6, 7 and 8) and Temperature (303, 313, 323 and 333) K were evaluated. The flask containing the samples were withdrawn from the shaker at predominant time intervals, filtered and the final concentration of CR dye was determining using the equation. The dye uptake capacity for each sample was calculated according to a mass balance using equation (1)

$$\text{Amount adsorbed } (q_e) = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

Where, m is the mass of adsorbent (g), v the volume of the solution (L), C_0 is the initial concentration of dye (mg /L), C_e is the equilibrium dye concentration (mg/L) and q_e is the amount of dye quantity adsorbed at equilibrium (mg/g). The percentage removal of dye from the solution was calculated by the following equation (2)

$$\% \text{ removal} = \frac{(C_0 - C_i)}{C_0} \times 100 \quad (2)$$

Adsorption Isotherm

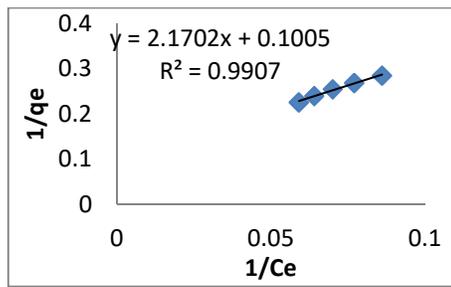
Two adsorption isotherms models were applied to describe the sorption equilibrium in the present study such as Langmuir and Freundlich isotherm model.

Langmuir Isotherm

The Langmuir sorption isotherm is applied to equilibrium sorption assuming monolayer sorption onto a surface with finite number of identical sites. The Langmuir equation is written as ¹³.

$$1/q_e = 1/q_m K_L C_e + 1/q_m \tag{3}$$

Where, q_e is the amount of dye adsorbed at equilibrium (mg/g), q_m is the amount of dye adsorbed when saturation is attained (mg/g), C_e is the equilibrium dye concentration (mg/L) and K_L is the Langmuir constant related to the binding strength of the dye onto the adsorption. The Langmuir model described the monolayer adsorption. It assumes a uniform energy of adsorption, a single homogenous layer of adsorbed solute at a constant temperature. Monolayer concentration increase with increase in temperature Fig. 2(a)



Freundlich Isotherm

The Freundlich isotherm is an empirical equation and is one of the most widely used isotherms for the description of multi site adsorption. The linear form as follows:

$$\text{Log } q_e = \text{log } K_F + 1/n \text{ log } C_e \tag{4}$$

Where, K_F and n are the Freundlich isotherm constants indicating the adsorption capacity and adsorption intensity respectively ¹⁴. The K_F and n can be calculated from the intercept and slope of the linear plot of $\log q_e$ against $\log C_e$. The significance of n is as follows; $n=1$ (linear), $n<1$ (Chemical process), $n>1$ (Physical process). The Freundlich constant is a heterogeneous factor and indicates that adsorption capacity increases with increase in temperature Fig. 2(b)

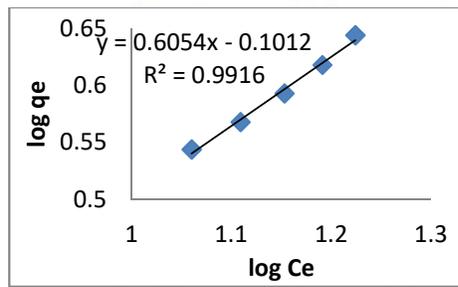


Fig. 2 (a) Langmuir adsorption isotherm (b) Freundlich adsorption model TPS CR

Table1. Characteristic parameter of the adsorption isotherm model for CR adsorbing by TPS

Models	Isotherms Constants	Results
Langmuir	q_m (mg/g)	10
	K_L (L/mg)	0.046
	R^2	0.990
Freundlich	$1/n$	0.605
	N	1.652
	K_F (mg/g)	-0.995
	R^2	0.991

Adsorption Kinetics

The Pseudo first order and Pseudo second order kinetic model were applied to study the adsorption kinetics of Congo red 4B dye to complete the extent of uptake in the adsorption processes.

Pseudo first order kinetic model

The linear form of the Lagergren's Pseudo first order kinetic model is represented by the rate equation (5)

$$\text{log}(q_e - q_t) = \text{log } q_e - \frac{k_1}{2.303} t \tag{5}$$

Where, q_e and q_t are the values of amount of the dye adsorbed per unit mass on the adsorbent at equilibrium and at various time t , respectively K_1 and calculated q_e can be from the slope and intercept respectively of the linear plot of $\log (q_e - q_t)$ versus t ¹⁵⁻¹⁶ Fig. 3(a). These plots are linear; however linearity of these curves does not necessarily assure first order

mechanism. Due mainly to the inherent disadvantages of correctly estimating equilibrium adsorption capacity the value obtained from the values; therefore first order kinetics is less likely to explain the rate processes.

Pseudo second order kinetics

The integrated form of the above model becomes,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

Where q_t is the amount of the adsorbed at contact time t (mg/g), q_e is amount of adsorbent adsorbed (mg/g) on the adsorbent at equilibrium. The initial adsorption rate h (mg.g-1min⁻¹) is expressed as, among these models the criterion for their applicability is based on judgment the respectively correlation coefficient (R^2) and agreement between experimental and calculated value of q_e Fig. 3(b) In

this model the rate determining step is biosorption mechanism involving chemisorptions, Where biosorbate removal from solution is due to physio chemical interaction between biomass biosorbate solution¹⁷.

Intra particle diffusion model

The intra particle diffusion model is expressed as,

$$q_t = K_{id}t^{1/2} + C \tag{7}$$

Where K_{id} is the amount of adsorbate time t (mg/g) and C is the variety of intercept (mg/g). A plot q_t versus $t^{1/2}$ gives a linear relationship from which k_{id} values is determined from slope and value of C intercept gives an idea about thickness of boundary layer¹⁵. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. Table 2

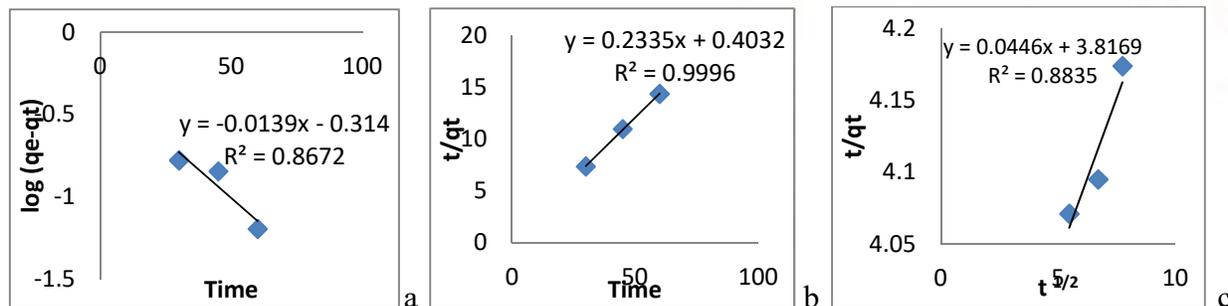


Fig. 3 (a) Pseudo first order (b) Pseudo second order (c) Intra particle diffusion kinetic models TPS CR

Table2. Characteristic parameters of the adsorption kinetic model for CR adsorbing TPS

Kinetic model	Parameter	Results
Pseudo 1st order	K^1 (min ⁻¹)	0.029
	q_e (mg/g)	0.686
	R^2	0.867
Pseudo 2nd order	h (mg.g ⁻¹ min ⁻¹)	2.481
	q_e (mg/g)	4.291
	R^2	0.999
Intra particle diffusion	K_{id}	0.053
	C	3.579
	R^2	0.937

Thermodynamic Parameter

The Thermodynamics parameter such as change in Gibbs’s free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined using the following equation. The Gibbs free energy ΔG equation expressed as following equation,

$$\Delta G^0 = -RT \ln K \tag{8}$$

$$\log K = \frac{\Delta S^0}{(2.303RT)} - \frac{\Delta H^0}{(2.303RT)} \tag{9}$$

Where K Equilibrium constant, R is universal gas constant (8.314 Jmol⁻¹K⁻¹) and T is temperature Kelvin, ΔS^0 and ΔH^0 are entropy and enthalpy respectively. The plot of $\ln K$ versus $1/T$ gives a linear respectively, which allows the computation of ΔS^0 and ΔH^0 values from the slope and intercept respectively.

For the negative ΔG^0 values indicates thermodynamically spontaneous nature of the adsorption. The decrease in ΔG values with increasing temperature shows on increase in feasibility of adsorption at higher temperature. The value of ΔH

was negative indicating that the nature of the adsorption is exothermic. The negative value of ΔS shows the decreasing randomness adsorbate solution interface during the adsorption process.

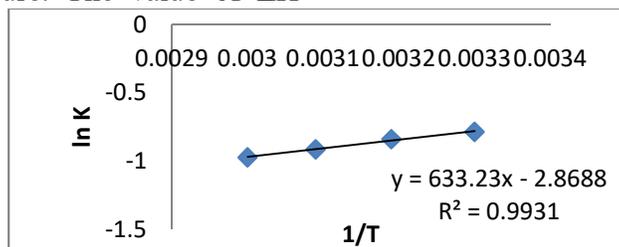


Fig. 4 Thermodynamic parameter $1/T$ vs. $\ln K$

Table 3. Thermodynamics parameter TPS CR

Temperature (K)	ΔG (J.mol ⁻¹)	ΔH (KJ.mol ⁻¹)	ΔS (J.mol ⁻¹ .K ⁻¹)	R ²
303	-1977	-12.123	-54.91	0.993
313	-2183			
323	-2451			
333	-2685			

RESULTS AND DISCUSSION

Adsorbent characterization

UV spectrum

UV visible spectrum of adsorption bond 495nm was noticed that the spectrum changes of adsorption bond may confirm the strong bond between the active group present in the inhibitor molecule and solid surface. It can be used for detect the absorbance value for the CR dye in different stages.

FTIR (Fourier Transform Infrared Spectroscopy)

The FTIR spectrum of TPS before and after adsorption Fig. 5 of CR dye were analyzed to determine the vibration frequency changes in their functional groups for TPS before adsorption various peaks at 500-3500cm⁻¹, Changes in the vibration and rotational movements of the molecule detection of functional groups which have specific vibration frequency. For example, C=O, NH₂, -OH etc.

Before adsorption of CR dye (3908.04cm⁻¹ and 3809cm⁻¹) from -OH hydroxyl groups, (3319.58 cm⁻¹ and 3249.57 cm⁻¹) N-H str from Amide groups, 3119.25 cm⁻¹ from NH₃⁺ Ammonium salts of carboxylic groups, 2915.41 cm⁻¹ C-H str from Alkanes, 2849.09 cm⁻¹ C-H str from Aryl and Aldehyde groups, 1736.95 cm⁻¹ C=C str from

Alkenes, 1628.90 cm⁻¹ C=O str from Ketones, 1440.89 cm⁻¹ C-H def from Diaryl and Dialkyl Esters. 1369.98 cm⁻¹ N-O str from Nitro compounds, -C-O str Alcohols, 1240.43 cm⁻¹ C-O str from Esters and Lactones, 1150.26 cm⁻¹ S=O str from Amine sulfides or Acids, 1017.46 cm⁻¹ Salts of phosphate esters, 800.62 cm⁻¹ N-H str from salts of Hydroxyl Halides, 690.39 cm⁻¹ C-S str from Sulphonic acids, 567.95 cm⁻¹ -NO₂ Aryl nitro compounds.

After adsorption of CR dye it was found that most of the functional groups the adsorbent were affected after the dye uptake process. This is judged from shifts in the position of some of the functional groups that moved at lower frequency or higher frequency or band intensity before and after CR adsorption includes 2913.50 cm⁻¹ C-H str from Alkanes, 2853.56 cm⁻¹ from C-H str from Alkyl groups, 1632.37 cm⁻¹ NH₃...SO₃⁻ from Amino sulfonic acids groups, 1525.40 cm⁻¹ Aromatic compounds, 1015.12 cm⁻¹ C-O str Carbohydrates, 554.01 cm⁻¹ Ar-X aryl halides halogen groups respectively indicates involving of these groups for CR binding to TPS.

SEM (Scanning Electron Microscopy)

Fig. 6 shows that SEM image of TPS powder it can be observed from the external surface of TPS powder is

very irregular with heterogeneous ridges and pores. SEM micrographs of TPS before and after adsorption are pictured in Fig. 6 respectively. The prepared TPS presents a micro porous structure with different pore diameters. In addition the TPS surface seems to be rough and presents many protrusions before

adsorption. This adsorption the TPS morphology has changed and the surface become smoother with less visible process, indication an adsorption on both the surface and within pores.

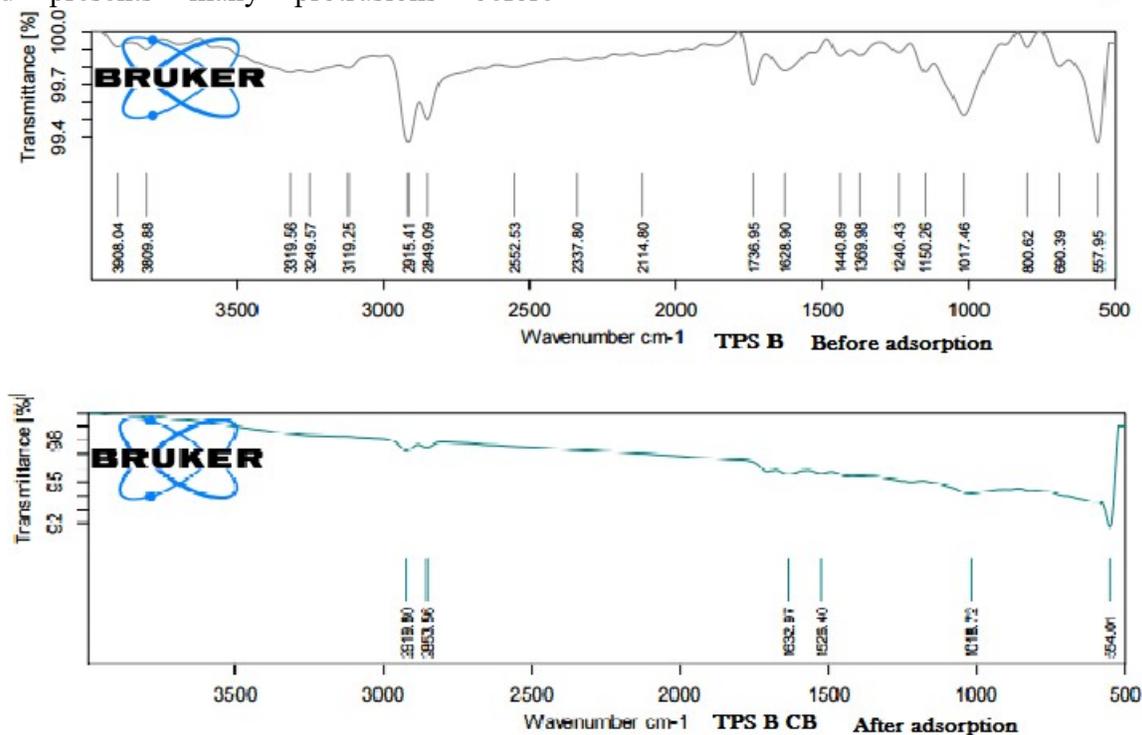


Fig. 5 FTIR Fourier Transform Infrared Spectroscopy for before and after adsorption on TPS CR

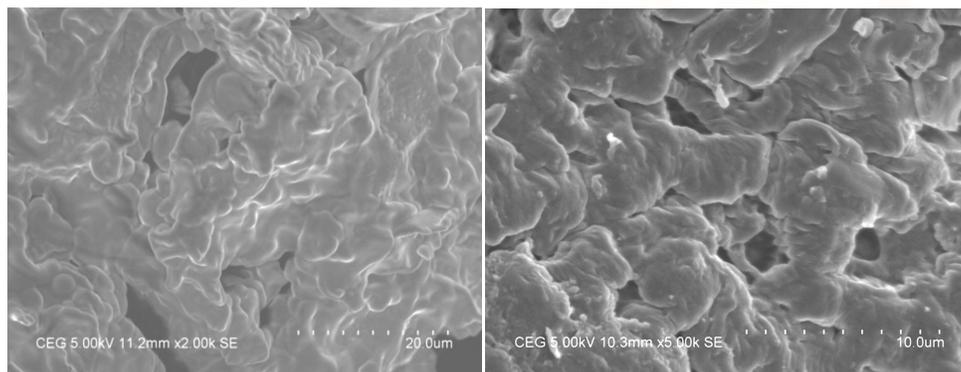


Fig. 6 SEM morphology image for TPS and TPS CR before and after adsorption

Influence of the Adsorption study

Effect of pH

The influence of pH on the adsorption of CR onto TPS is illustrated in Fig 7a it was observed that the percentage removal and adsorption capacity of CR by TPS decrease as pH increase from 3 to 8 optimum sorption was obtained at pH 3. The decrease in percentage removal and adsorption capacity with

increase in pH can be attributing for the adsorption sites on the adsorbent surface while the anionic groups of the CR dye for the adsorption sites on the adsorbent surface while at low pH values the negative charge (-OH) in the solution decrease and the adsorption surface is more positively charged thus enhancing attraction of the anion of the CR dye.

Effect of adsorbent dosage

The effect of adsorbent dosage as the percentage of CR dye as shown in Fig.7b it can be observed that the

percentage of CR dye increased with increase in the adsorbent dosage. Although, the equilibrium adsorption capacity decreased with increase of adsorbent dosage. This is may be due to aggregation of the adsorption sites which limits the availability of all the active sites during adsorption process.

Effect of Initial dye concentration

The effect of initial dye CR concentration depicted in Fig. 7c It can be observed that the percentage removal of CR dye decrease with increase in initial concentration. This is due to the fact increase in dye concentration more dye molecules are available for adsorption by the adsorbent. This is attributes to the effects of concentration gradient which is the main deriving forces for the adsorption process. As the initial concentration increase, the available site on adsorbent surface area becomes less which causing increment in dye being adsorbed. However, these removal dyes percentage decrease. Which is been proved in Fig. 7c the experimental data showed of CR adsorbed decrease in particle size of the adsorbent. This indicated that the smaller TPS particles see for a given mass of TPS the more surface area is available and as a consequence the greater number of binding sites available.

Effect of Contact time

The effect of contact time on the removal of CR dye is depicted in Fig. 7d it can be observed that there was a rapid removal in the first 30 minute and it proceeds slowly until result has been reported for the adsorption of CR onto TPS powder. It can be inferred from the rapid sorption rate at the initial stage that there were great quantity of active site on the external surface of TPS which resulted in the swift CR dye removal. Once equilibrium is attained there was further increase since the remaining vacant sites are difficult to occupy probably due to the adsorbents and the bulk phase.

Effect of Temperature

The influence of temperature of the percentage removal of CR dye TPS is illustrated in Fig. 7e it can be observed the increase in temperature resulted in decreased in percentage removal of CR by TPS. This decrease in removal efficiency with increase in temperature can be attribute to the weakening of the physical bonding between the adsorbent CR dye and the active sites of the adsorbent (TPS). In addition the CR dye solubility also increases with increase in temperature resulting in the interaction between the solute and the solvents to be stronger than that between the solute was more different to adsorbed.

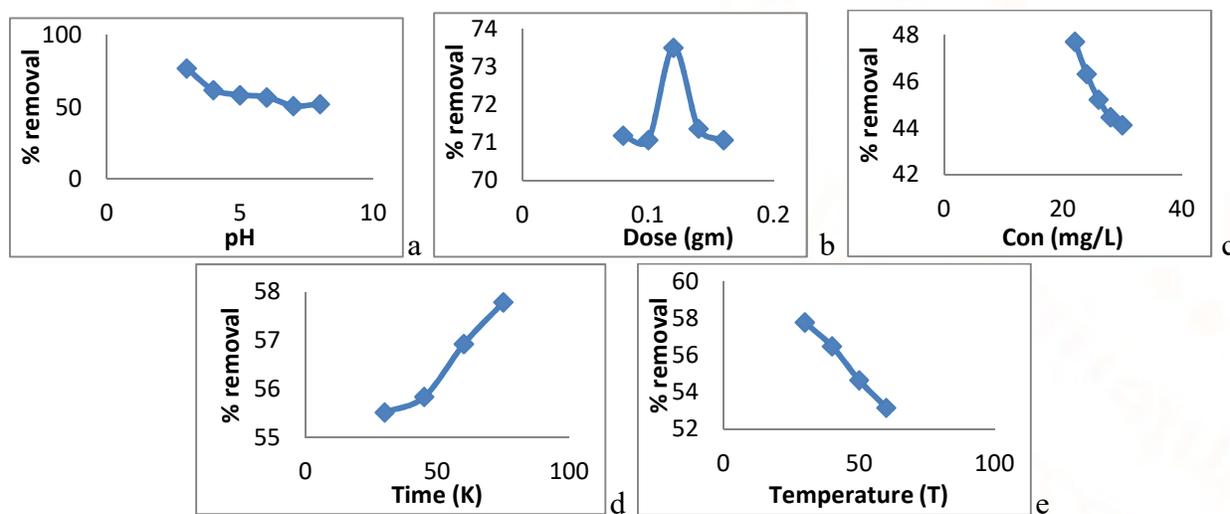


Fig. 7 Effects of (a) pH, (b) Adsorbent dosage, (c) Initial dye concentration, (d) Contact time, (e) Temperature TPS CR

CONCLUSION

Dyes are generally present in the effluents of textile industries. They are distribute in soils aquatic environment and are known to be a source of environment contaminates so the necessary demands to focus the attention on technique leading to complete removal of dye molecule. The removal of

Congo red 4B from industries wastewater using biomass (TPS) has been investigated under different experimental conditions. The adsorbing of CR dye was examined at different experimental conditions. The results corrugate that adsorption increase in increase contact time, temperature, adsorbent dosage

and pH. The maximum removal of dye CR at 303K was found to be 57.73% for TPS, 75min⁻¹ was found to be 57.79%, 22mg/L was found to be 47.72%, 0.12g was found to be 73.51% and pH was found to be 77.74% at maximum percentage removal in this study. Kinetic study shows the adsorption reaction follows Pseudo second order kinetic model ($R^2=0.999$). The equilibrium data were found to be well represented by Freundlich isotherm shows that the surface is heterogeneous in nature. The percent research work established that TPS was excellent low-cost bio adsorbent for the removal of dye CR. The negative values of ΔG^0 and the negative value of ΔH^0 obtained indicated the spontaneous and exothermic nature of the adsorption process while the negative ΔS^0 value obtained decreased randomness during the adsorption process. The kinetic and thermodynamic data can be Further explore for the design of an adsorbed for industrial effluents treatment.

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