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Effective Removal of Turquoise Blue Reactive Dyes using Tubular Furnace Supported Activated Carbon Prepared from *Delonix regia* Pods-kinetics and Thermodynamic Studies

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ABSTRACT

This investigation explores "batch adsorption of turquoise blue dye" from aqueous solutions using phosphoric acid-activated "*Delonix regia* Pod carbon prepared using a tubular furnace" (DRTFC). Various factors were examined and equilibrium data were gathered at different temperatures (205 K, 315 K, and 325 K) and for varying initial dye concentrations. Optimal pH for dye removal was found to be 2. Kinetic modeling was done using "Lagergren's first-order kinetics", Ho's "second-order kinetics", and Weber Morris equations, with the "pseudo-second-order kinetic model" showing the best fit based on Sum of Squared Errors (SSE) analysis. Thermodynamic parameters were determined through "Van't Hoff plots", suggesting that the adsorption process was endothermic, spontaneous, and with increased randomness.

Keywords: Adsorption, Turquoise Blue dye, H_3PO_4, *Delonix regia* Pods, Kinetics and thermodynamics.

INTRODUCTION

Throughout the dyeing process, over 15% of the world's total dye production is wasted and emitted as influents[1]. One of the most challenging tasks facing the pulp, paper, textile finishing, and dye production industries is the removal of colour from such wastes. Basic dyes are cationic dyes that dissolve in water and are mostly used on acrylic fibres, though they can also be used to colour wool and silk[2]. Among all the dyes in its category, turquoise blue dye (IB), a basic dye, is commonly used for "dying cotton, wool, silk, nylon, paper, leather", etc.

In comparison to every other dye in its class, with very high tinctorial values, basic dyes are the brightest class of soluble dyes; less than 1 milligram per liter of the dye results in a noticeable coloration.

As a result, it is important to remove colours from waste water before discharging into water

sources. Waste water can be treated using a variety of techniques to remove dyes. Electrochemical oxidation[3], photodegradation[4], electrocoagulation[5] and membrane filtration[6] and Adsorption[7] are a few of them. Adsorption has emerged as the most effective approach among these to treat wastewater. The removal of colours from wastewater has been effectively accomplished using adsorption employing activated carbon as an adsorbent[8]. A variety of agricultural waste products, such as sawdust, sunflower seeds, tamarind fruit shells, coir pith, and cashew nut shells, are utilized as precursors to prepare activated carbon.

This study investigates the viability and effectiveness of using *Delonix regia* Pods in adsorption methods to extract the cationic dye Turquoise Blue dye from artificial aqueous solutions. To learn more about the adsorption properties of *Delonix regia* Pods, researchers looked at the impacts of temperature, adsorbent dose, adsorbate concentrations, and contact time.

Symbols and Subscripts

C_i, C_t and C_e	"Initial Conc. of TB dye soln., at the time 't' and at equilibrium respectively"
q_e & q_t	"Quantity adsorbed at the equilibrium 't' at time respectively"
'V'	"Volume of the TB dye soln in liter (L)"
'W'	"Mass of a carbon" in (g)
'R'	"Gas Constant"
'T'	"Temperature" (K)
'k_1'	"First-Order rate constant" of adsorption (l/Min)
'k_2'	"Second-order rate constant"
'T'	"Time in minutes"
'h'	"Initial adsorption rate" (milligram per liter min)
'kp'	"Intra-particle diffusion rate constant"
'C'	"Thickness of the boundary film"
'N'	"No. of data points"
'Kc'	"Equilibrium constant"
'$\Delta G°$'	"Standard free energy"
'$\Delta S°$'	"Entropy of adsorption"
'$\Delta H°$'	"Enthalpy of adsorption"

Tools for Processing Data

S. No	Framework	Formulae
1 Mass balance relationships	% of Removal	"$(C_i-C_t)\times V/C_i$
	Quantity adsorb. at equilibrium, q_e	$(C_i-C_e) \times V/W$
	Quantity adsorb. at the time t, q_t	$(C_i-C_t)\times V/ W$"
2 Kinetic Models & SSE %	Pseudo First order kinetics[9]	
	(Legergren equation)	"$\log (q_e-q_t) = \log q_e-k_1/2.303\times t$
	Pseudo Second order kinetics[10]	$t/q_t = 1/k_2.q_e^2+1/q_e\ t$
	(Ho equation)	
	The initial adsorp. rate is h	$h = k_2q_e^2$
	Intra particle diffusion[11]	$qt = kpt^{1/2}+C$
	(Weber–Morris equation)	
	Sum of error square	SSE (%) = $\sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2/N}$"
3 Thermodynamic Parameters	Standard Free energy Change	$\Delta G° =-RT \ln K_c$
	"Van't Hoff equation"[12]	$\ln Kc = \Delta S°/R-\Delta H°/RT$

MATERIALS AND METHODS

Composition of adsorbate

The dye stock solution was made using Analar grade turquoise blue dye, which was dissolved to concentration of 1000 milligram per liter in double-distilled water using an appropriate amount of precisely weighed dye. By carefully diluting the stock solution, the experimental solutions were created.

Preparation of Adsorbent

To get rid of any surface dust, distilled water was used to wash the *Delonix regia* leaves. After that, they were sun-dried, cut into tiny pieces, and processed with a pulverizer into a powder. One hundred millilitres of a 60% H_3PO_4 solution and fifty grammes of pod powder were mixed together and allowed to sit at room temperature for a full day. After that, the materials were heated for two hours at 800°C in a nitrogen environment at a rate of 1°C per minute. After that, the carbon sample were cleaned with 0.5 M HCl and deionized water until the washing liquid's pH reached 7.0, which is neutral. After that, the material was dried for an hour at 383 K in a hot oven. Ultimately, the dehydrated material was crushed and filtered to produce particles with an average size between 150 and 300 µm. *Delonix regia* Pod Activated Carbon is the name given to this processed material (DRTFC).

Batch adsorption experiments

The "adsorption of turquoise blue dye on DRTFC" investigated by manipulation of multiple process factors, like 'temperature', 'adsorbent ratio', 'contact time', and 'initial dye concentration'. A predetermined amount of DRTFC was added 50 millilitres of the "dye solution". A mechanical shaker running at 180 rpm was used to fully agitate the mixture for the predetermined amount of time. The solution was then centrifuged, and using a 'Systronics 2202 UV-Visible spectrophotometer', the remaining colour in the centrifuged solution was measured spectrophotometrically at a wavelength of 780 nm.

"Kinetic models" were applied and experimental data about the initial dye concentration and contact time were used for assessment.

RESULTS AND DISCUSION

Effect of adsorbent dosage

Adsorbent dosages of 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 Mg were added to 50 ML of "dye solution" at a 50 milligram per liter concentration to conduct the investigation. Fig. 1 illustrates how the percentage of dye removed from an aqueous solution rises as the carbon dose raises. This is because there are more adsorption sites and a larger surface area of carbon[13,14]. The homogeneous adsorbing sites are indicated by the smooth curve. These findings led to the adsorbent dose of 40 mg/50 mL being used for the following experiments, which gave a removal percentage of 71.02%.

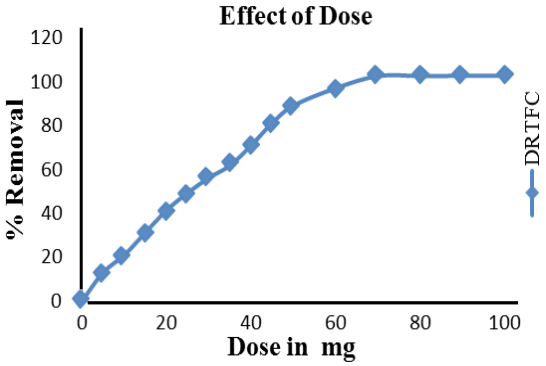

Fig. 1. [TB dye]:50 Milligram per liter; Contact time: 160 Min; PH:2

Impact of duration of contact

The starting concentrations for this investigation were 25, 50, and 75 mg/L solutions. The findings are displayed in Fig. 2. At first, the proportion of dye removed increases quickly as contact duration increases; after that, it increases gradually, and after 100–180 min, no discernible change is seen. It was discovered that when the original concentration of dye solution increased, the percentage of dye dropped.

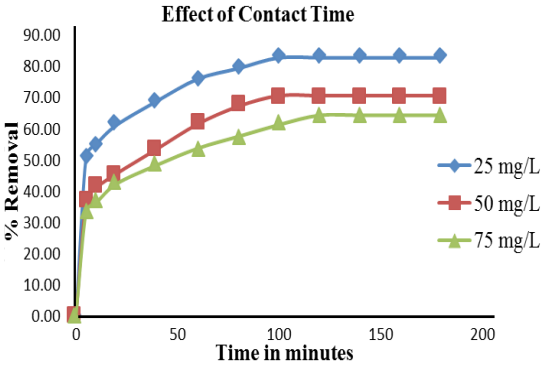

Fig. 2. [TB dye]: 50 Milligram per liter; Dose: 40 Milligram per liter; PH: 2; T: 305K

Adsorption dynamics

Kinetic studies are needed to define reaction mechanism of adsorption process. Different kinetic models like "pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models" were analyzed in the adsorption of TB dye onto DRTFC.

Pseudo first–order kinetic model

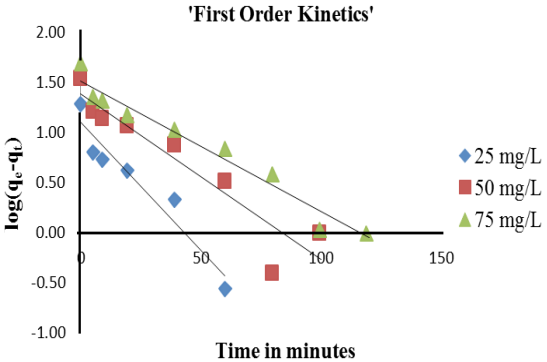

Fig. 3. [TB dye]: 50 Milligram per liter; Dose: 40 Milligram per liter; pH: 2; T: 305K

Table 1: Pseudo first order Kinetics results for TB dye ontoDRTFC [PH = 2; Dose = 40 Milligram per liter 50 Milli Liter; Agitation time = 180 min; Temp = 305K]

	"Pseudo First Order Kinetics"					
Initial Conc. C_i (Mg/L)	k_1(min^{-1})	$q_{e,cal}$ (mg g^{-1})	$q_{e,exp}$ (mg g^{-1})	Δq_e	R^2	MSSE
25	0.0339	12.3537	20.74	-8.38	0.8776	3.97
50	0.0320	25.5035	35.4	-9.89	0.9692	
75	0.0272	33.9938	48.38	-14.38	0.9631	

Pseudo–second order kinetic model

The data obtained for "adsorption kinetics" was further analyzed employing "pseudo first order" and the "pseudo second order models". Additionally, the initial concentrations of adsorbate had a substantial positive correlation with the first phase of adsorption. The results for the 'R^2 values' for the "pseudo-first-order" model were between 0.995 and 0.997, and for 'R^2 values' for the "pseudo-second-order model" were between 0. 998 and 0. 999. In order to choose the most suitable model the theoretical uptake ($q_{e,cal}$) obtained from the models was compared with the experimental q_e ($q_{e,exp}$). The model that has the greatest number of elements with approximate $q_{e,cal}$ values to the $q_{e,exp}$ values is said to be the best fit model. This is measured by the Mean Sum of Squared Error (MSSE), and smaller values are more desirable, suggesting a more accurate model. The "pseudo-second-order model" yielded lowest MSSE and hence, most appropriately described the adsorption data, thereby underlining that it was the most suitable model for describing the adsorption kinetics. The low diff. between $q_{e,cal}$ and $q_{e,exp}$ as compared to the "pseudo-first-order kinetic model" defines that the present model is better.

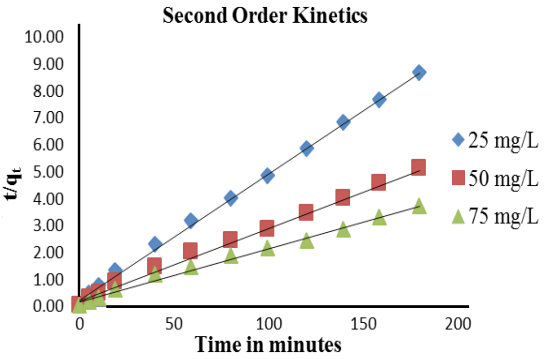

Fig. 4. [TB dye]: 50 Milligram per liter; Dose: 40 Mg/L; pH: 2; T: 305K

Table 2: Pseudo second order Kinetics results for TB dye onto DRTFC [PH = 2; Dose = 40 Milligram per liter 50 MilliLiter; Agitation time = 180 min; Temp = 305K]

	Pseudo Second Order Kinetics						
Initial ConcentrationC_i (mg/L)	k_2(g mg^{-1} min^{-1})	$q_{e,cal}$(mg g^{-1})	$q_{e,exp}$(mg/g)	Δq_e	'h' (mg/g min)	R^2	MSSE
25	0.0092	21.3675	20.74	0.6275	4.2088	0.9984	0.74
50	0.0035	37.0370	35.4	1.6370	4.7348	0.996	
75	0.0022	50.5050	48.38	2.1251	5.7013	0.9949	

Intraparticle diffusion model

In the prior research it has been proved that the adsorption process is a multistep event here the molecules of solute are transferred from the fluid phase to the surface of adsorbent and then to the inside of the pores and this stage is usually slow[15-18]. The multilinearity of the qt versus $t^{1/2}$ plots also supports the population of these phases in the adsorption mechanism. As revealed by the slope and intercept values separately estimated in this study (Table 3), the kp and C values suggest that the adsorption rate constants are higher at higher initial dye concents. This indicates that a significant factor influencing the total rate of the "adsorption process" is the rate of dye diffusion within the sorbent particles' pores.

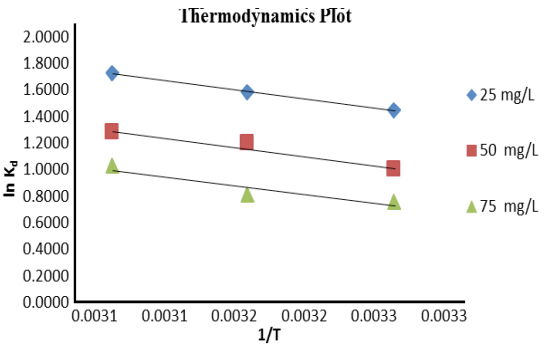

Fig. 5. [TB dye]: 50 Milligram per liter; Dose: 40 Milligram per liter; PH: 2; T: 305K

Table 3: Intra Particle Diffusion results for TB dye on DRTFC [PH = 2; Dose = 40 Milligram per liter 50 milliliter; Agitation time = 180 min; Temp = 305K]

	Intra Particle diffusion		
Initial Concen. C_i (milligram per liter)	C (mg g^{-1})	k_p (mg g^{-1} min^{-1})	R^2
25	10.269	1.1239	0.9976
50	11.943	2.4158	0.9943
75	20.214	2.5959	0.9986

Adsorption thermodynamics

The "Van't Hoff" plots demonstrate a high linearity of ln Kd against 1/T. The ΔG° values are obtained utilizing the Kd and T data analysis. From the plots of log [K] against 1/T. The "enthalpy (ΔH°) & entropy (ΔS°)" changes are calculated by the intercepts and slopes respectively as shown in the Table 4 and Figure 6.

In all the tested systems, the ΔG° values are negative, which support the occurrence of the favorable and spontaneous adsorption processes. The positive ΔH° values imply the endothermic process and values of 1–93 kJ mol^{-1} support the view that physisorption is the main mechanism (Author, Year). Positive ΔS° values signify an increase in unpredictability, particularly near the interface between the "solid-solution." Because adsorbate species use a portion of translational entropy, their displacement of water molecules is likewise linked to increased randomness[19-21]. Higher temperatures may increase the size of pores and stimulate activity on the adsorbent surface and improve its adsorption ability.

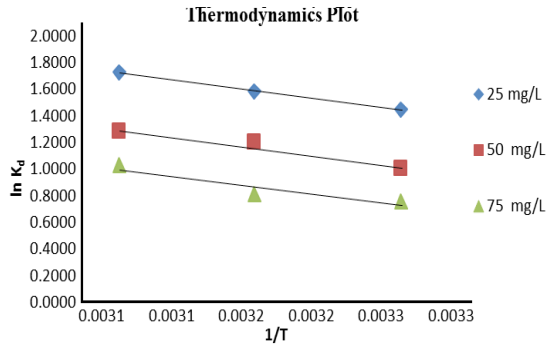

Fig. 6. Plot of ln Kd vs 1/T

Table 4: Thermodynamic parameters of TB dye by Delonix Regia Pods

C_i(mg/L)	Δ ΔG (kJ mol^{-1}) 303 K.	313 K.	323 K.	ΔH (kJ mol^{-1})	ΔS (Jk^{-1} mol^{-1})
25	-3.6674	-4.1430	-4.6646	-11.532	49.8092
50	-2.4983	-3.1532	-3.4117	-11.49	46.0845
75	-1.9029	-2.1372	-2.7570	-11.049	42.2933

CONCLUSION

In a recent study, the feasibility of using carbon activated with phosphoric acid derived from pods of Delonix Regia was investigated for the removal of a "turquoise blue dye" from water. In batch adsorption studies, it was observed that the activated carbon could remove the dye efficiently to a significant amount. The equilibrium was attained in 100-180 min using 40mg of adsorbent for every 50 mL of solution at 305K. The optimum pH for adsorption was 2 for initial dye concentrations of 25-75 mg/L. The results of the kinetics analysis showed that the "pseudo second-order kinetics" best described the adsorption process and "intraparticle diffusion" was the major role play in the mechanism. "Thermodynamic studies" suggested that the adsorption process was spontaneously endothermic with increased randomness.

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Conflict of interest

The author declares no conflict of interest

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