Adsorption of Reactive Dyes from Aqueous Solution Using Activated Carbon Prepared from Plantain Leaf Sheath Waste



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All parts of the plantain are widely used in India for various purposes. But plantain leaf sheath always ends up as waste material which accumulates as a biowaste. The present study focuses on the preparation of activated carbon using phosphoric acid as activating agent, and its efficacy as an adsorbent for the removal of reactive dyes, Reactive Green 19, and Reactive Red 141. Batch adsorption studies have been conducted and optimum adsorption conditions were determined as a function of contact time, initial dye concentration, adsorbent dosage, and pH. The experimental data were analyzed using Langmuir, Freundlich and Temkin isotherm models. The pseudo-first and second-order, intraparticle diffusion, and Elovich models were used to analyze the kinetic parameters of the adsorption system. Under the optimum conditions (initial dye concentration = 200 mg L⁻¹, adsorbent dose = 1 g, pH = 2, contact time = 220 min for reactive green 19 and 180 min for reactive red 141), maximum percentage removal for reactive green 19 and reactive red 141 were obtained as 65.9 % and 72.7 %, respectively. The results demonstrate that activated carbon produced from chemical activation of the plantain waste has the potential of adsorbing reactive dyes from industrial effluents.

Keywords:

plantain waste, activated carbon, reactive green 19, reactive red 141, isotherm and kinetic models

Introduction

Textile industry dyes have a synthetic origin and complex chemical structure. Basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes, and sulphur dyes¹ are the different types of dyes used. During the dyeing process, the competition between the colouring reaction and the hydrolysis of the reactive group results in a loss of unfixed dye of approximately 20 to 25 %, which leads to the production of coloured effluents².

Water pollution from the dyeing industry is a matter of great concern, since a large quantity of effluents are discharged directly into the water bodies. The dye effluent is highly toxic in nature³. Major problems associated with colour effluent include lowering light penetration, photosynthesis, and damage to the aesthetic nature of the water surface⁴⁻⁶. Moreover, their degradation products may be mutagenic and carcinogenic^{7,8}. Many dyes may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive, and central nervous system⁹.

Reactive dyes are formed by the combination of azo-based chromophores with different types of reactive groups, like vinyl sulphone, chlorotriazine, etc. Reactive dyes are commonly used in textile industries because of their favourable characteristics of bright colour, water-fastness, and simple application techniques with low energy consumption¹⁰.

The current techniques used for the removal of dyes include adsorption, filtration, Fenton's oxidation method, ozonization, solvent-extraction method, coagulation/flocculation, ion exchange, and bioremediation^{11–13}. Among them, adsorption is effective and cheap when compared with other methods. Activated carbon, a broad-spectrum adsorbent, is capable of removing a wide range of pollutants from water. Activated carbon is a porous material that behaves as a powerful adsorbent because of its high surface area, adequate pore size distribution, and variable characteristics of surface chemistry, low ash content, and relatively high mechanical strength¹⁴. One of the major drawbacks is the reusability of activated carbon. Around 10-15 % of activated carbon is lost during the regeneration process, which in turn increases the overall cost of the treatment process. Therefore, preparation of activated carbon from cheaper materials, such as agricultural wastes, has gained great attention¹⁵.

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Agricultural waste is considered a rich source for activated carbon production. The use of agricultural waste as activated carbon precursors depicts a renewable and relatively less expensive route¹⁶. Preparation of activated carbon from agricultural waste materials, like wheat, corn-straw, sugarcane bagasse, cotton refuse, oat hull, almond shells, apricot-stones, corn cob, corn hull, cotton stalks, rice hull, rice husk and rice straw has been reported previously¹⁷. The mechanism of adsorption using activated carbon is represented in Fig. 1.

Plantain is one of the world's oldest fruit crops of the family *Musaceae*, cultivated widely in the tropical and subtropical regions of the world^{18,19}. The world's leading plantain producers are India, China, Uganda, Ecuador, Philippines, and Nigeria²⁰. According to Indian Horticulture Database, plantain is cultivated over an area of 884 ('000 Ha) and production was reported to be 30808 ('000 MT) for the year 2017–18. The huge quantities of biomass generated by plantain farming go as waste due to non-availability of suitable technology for its com-

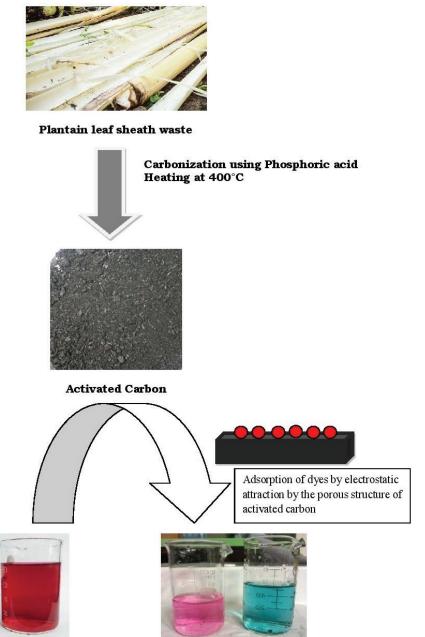


Fig. 1 - Adsorption mechanism

Decolorized dye

mercial utilization²¹. Though plantain leaf sheath is used for fibre production, a large quantity of it is dumped or burnt, hence causing environmental pollution.

Only a few studies have been reported in the literature for the adsorption of reactive dyes (Table 3). In this research study, activated carbon was prepared from plantain leaf sheath waste using phosphoric acid activation. The prepared activated carbon was characterized by SEM and FTIR. Adsorption isotherm and kinetics have been studied for the dyes- Reactive red 141 and Reactive green 19.

Materials and methods

Materials

Adsorbent

Plantain leaf sheath waste used for the preparation of adsorbent was collected from a local market in Chennai, Tamilnadu.

Adsorbate

Reactive Green 19 and Reactive Red 141 dyes are used as adsorbates in this study. The dyes were procured from the commercial textile industry at Tamilnadu. The details of the reactive dyes are presented in Table 1.

Preparation of the adsorbent

The collected agro-waste was washed thoroughly with distilled water and oven-dried at 40 °C to obtain constant weight. The samples were ground and stored in polyethylene bags. Activated carbon was prepared according to the method in the literature²² with slight modifications. The samples were treated with orthophosphoric acid (Merck, Emparta®, 88 %) in the ratio of 2:1 (w/v). Samples were kept at room temperature for 24 hours, and the resulting slurry was dried at 100 °C in a hot air oven. After drying, the sample was washed with distilled water until a constant pH was reached, and dried again in a hot air oven. Carbonization and activation was done by heating the dried carbon in a preheated muffle furnace at 600 °C for one hour. The end product was stored in airtight containers for further analysis.

Characterization of the adsorbent

Scanning electron microscopy (Carl Zeiss MA15/EVO 18 Scanning Electron Microscope, Germany) was used to visualize the surface morphology of the prepared activated carbon. The samples were coated with gold by a gold sputtering device for a clear vision of the surface morphology. The surface distributions were collected from SEM pictures using different magnifications. FTIR spectra was recorded in the range of 4000–650 cm⁻¹ at a

Table 1 – Details of dyes

S.No.	Dye	Synonyms	Molecular formula	Molecular weight	$\lambda_{ m max}$	Structure	Reference
1	Reactive Green 19	Reactive Green HE4BD, Procion Green HE4BD	$C_{40}H_{23}Cl_{2}N_{15}Na_{6}O_{19}S_{6}$	1418.94 g mol ⁻¹	630 nm	NaO ₃ S N-N H SO ₃ Na NaO ₃ S N-N H CI NaO ₃ S N-N H SO ₃ Na NaO ₃ S N-N H SO ₃ Na	46
2	Reactive Red 141	Reactive Red HE7B, Procion Red HE7B	${\rm C}_{52}{\rm H}_{26}{\rm Cl}_2{\rm N}_{14}{\rm Na}_8{\rm O}_{26}{\rm S}_8$	1774.19 g mol ⁻¹		NaO ₃ S - SO ₃ Na H NaO ₃ S - SO ₃ Na NaO ₃ S N SO ₃ Na SO ₃ Na	47 ⊙₃Na

resolution of 4 cm⁻¹ using a Diamond ATR (Agilent CARY 630 FTIR Spectrometer). Ash content, moisture content, and volatile matter content were calculated by following the methods suggested by the European Council of Chemical Manufacturers' Federations²³. Iodine number, methylene blue number, and pH drift (pHpzc- point of zero charge) were determined using appropriate methods in the literature^{24,25}. The surface area of activated carbon was determined from the iodine number²⁶.

Adsorption experiments

Adsorption equilibrium and kinetics were determined by the batch method. Adsorption isotherms were performed using dye solutions of different initial concentrations (100–500 mg L⁻¹). Equal masses of 1 g of activated carbon were added to dye solutions. The flasks were agitated at 150 rpm for 300 min to ensure the system has reached equilibrium. Samples were collected and centrifuged at 3000 rpm for 10 min. The supernatant was analyzed using a UV-vis spectrophotometer (GENESYSTM 10S).

The percentage removal of dye from solution and the equilibrium adsorption capacity (Q_e) was calculated by the following equations (1) and (2):

Removal efficiency (%) =
$$((\gamma_i - \gamma_e)/\gamma_i) \cdot 100$$
 (1)

Equilibrium adsorption capacity,
$$Q_{\rho} = (\gamma_{i} - \gamma_{\rho}) \cdot V/m$$
 (2)

where Q_e is the amount of dye adsorbed at equilibrium (mg g⁻¹), γ_i and γ_e are the initial and equilibrium concentrations of the sample (mg L⁻¹), m is the mass of adsorbent (g), and V is the volume of the sample (L), respectively.

The kinetic experiments were studied using an initial dye concentration of 200 mg L⁻¹. One gram of activated carbon was added to the dye solutions and the solution was agitated at 150 rpm. Aliquots were drawn at every 20 min, centrifuged, and analyzed. The adsorption capacity at different time intervals (Q_t) was calculated by the following equation-

$$Q_{t} = (\gamma_{t} - \gamma_{t}) \cdot V/m \tag{3}$$

Along with isotherm and kinetic experiments, the effect of adsorbent dosage on adsorption (0.5 g-2.5 g) was analyzed using 200 mg L^{-1} as initial dye concentration.

Adsorption isotherms

To study the adsorption pathway and equilibrium relationship between the amount of dye adsorbed by activated carbon and the amount of dye present in the solution, it is essential to design adsorption isotherms. Isotherms predict the appropriate parameters and behaviour of sorbent towards different sorption systems²⁷. In this study, Langmuir, Freundlich and Temkin isotherm models were used to investigate the adsorption equilibrium between the dye solution and the activated carbon phase.

Langmuir isotherm

The Langmuir model is a non-linear model that suggests a monolayer uptake of the adsorbate on a homogeneous surface, having uniform energies of adsorption for all the binding sites with no interaction between the adsorbent molecules²⁸. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$\gamma_e/Q_e = (1/K_L \cdot Q_{\text{max}}) + (\gamma_e/Q_{\text{max}}) \tag{4}$$

where γ_e is the equilibrium concentration (mg L⁻¹), and Q_e is the amount of dye adsorbed at the equilibrium (mg g⁻¹), $Q_{\rm max}$ (mg g⁻¹) and $K_{\rm L}$ (L mg⁻¹) are the Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

The Langmuir parameters can be used to predict the affinity between the adsorbate and adsorbent using dimensionless separation factor $(R_{\rm L})^{13}$. $R_{\rm L}$ is calculated by the following equation.

$$R_{\rm r} = 1/(1 + K_{\rm r} \cdot \gamma_{\rm o}) \tag{5}$$

The value of $R_{\rm L}$ indicates the shape or nature of the isotherm. Depending on the $R_{\rm L}$ value, the isotherm can be unfavourable $(R_{\rm L} > 1)$, favourable $(0 < R_{\rm L} < 1)$, linear $(R_{\rm L} = 1)$ or irreversible $(R_{\rm L} = 0)$.

Freundlich isotherm

The Freundlich isotherm is an empirical model that is based on adsorption on the heterogeneous surface and active sites with different energy²². The linearized Freundlich isotherm is represented by the following equation:

$$\log Q_e = \log K_F + (1/n) \log \gamma_e \tag{6}$$

where K_F is a constant related to bonding energy which can be defined as the adsorption or distribution coefficient, and 1/n is adsorption intensity that indicates the type of isotherm to be irreversible (1/n = 0), favourable (0 < 1/n < 1), and unfavourable (1/n > 1).

Temkin isotherm

Temkin isotherm considers the effects of indirect adsorbent-adsorbate interactions on adsorption isotherms. The isotherm is based on two assumptions- i) The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interactions, and ii) the adsorption is characterized by a uniform distribu-

tion of binding energies¹³. The linearized Temkin isotherm is represented by the following equation:

$$Q_e = B \ln K_{\rm T} + B \ln \gamma_e \tag{7}$$

where $K_{\rm T}$ is Temkin constant related to the equilibrium binding energy (L mg⁻¹), $B = RT/b_{\rm T}$, $b_{\rm T}$ is Temkin constant related to the heat of adsorption (J mol⁻¹).

Kinetic studies

Kinetic studies provide necessary information about optimum conditions, mechanism of sorption, and possible rate-controlling step²⁹. In this study, pseudo-first and second-order, intraparticle diffusion, and Elovich kinetics were applied to adsorption data.

Pseudo-first-order kinetics

The pseudo-first-order kinetic model of Lagergren is given by the following equation³⁰.

$$\ln(Q_{o} - Q_{t}) = \ln Q_{o} - K_{1}t \tag{8}$$

where Q_e is the quantity adsorbed at equilibrium (mg g⁻¹), and Q_t is the quantity absorbed at time t (mg g⁻¹). K_1 is the rate constant for the pseudo-first-order sorption (min⁻¹).

Pseudo-second-order kinetics

The pseudo-second-order kinetics for adsorption system is analyzed based on the following equation³¹.

$$t/Q_{t} = 1/Q_{a}^{2} \cdot K_{2} + t/Q_{a} \tag{9}$$

where Q_t is the amount adsorbed at time 't', Q_e is the equilibrium amount adsorbed, 't' is time in min, K_2 is the rate constant of pseudo-second-order model.

Intraparticle diffusion model

According to the intraparticle diffusion model, the adsorbate uptake Q_t varies almost proportionally with the square root of the contact time, $t^{1/2}$ as given by the following equation

$$Q_t = K_p t^{1/2} + C {10}$$

where Q_t is the amount adsorbed at time t, and K_p is intraparticle diffusion rate constant.

The plot of uptake, Q_r , versus the square root of time $(t^{1/2})$ should be linear if intraparticle diffusion is involved in the adsorption process, whereas, if these lines pass through the origin then intraparticle diffusion is the rate-controlling step. Conversely, if the plots do not pass through the origin, it indicates

some degree of boundary layer control and it further shows that the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously³³.

Elovich model

The Elovich kinetic model in its linear form is expressed by the following equation³⁰.

$$Q_t = \beta \ln (\alpha \beta) + 1/\beta \ln t \tag{11}$$

where Q_t is the quantity of adsorbate adsorbed at time t (mg g⁻¹), α is a constant related to chemisorption rate, and β is a constant depicting the extent of surface coverage.

Desorption studies

Desorption is a phenomenon whereby a substance is released from or through a surface. The study was performed to assess the regeneration capacity of the adsorbent. Regeneration and reuse of adsorbent is an important criteria required in order to make the process economic and environmentally friendly. The dye loaded activated carbon was centrifuged in order to separate carbon from the slurry.

The separated activated carbon particles were then brought into contact with 250 mL of the regenerants with desired concentrations (0.2 N to 1.0 N NaOH), and then shaken at 150 rpm for 2 h for regeneration. After filtration, the dye concentrations in the solutions were measured to calculate the amounts of dye remaining in the activated carbon. The desorption efficiency was then calculated by the following equation:

Desorption efficiency (%) =
$$((C_0 - C_d)/C_0) \cdot 100$$
 (12)

where C_0 and C_d are the originally adsorbed amount, and residual adsorbed amount of the dye after desorption, respectively.

Results and discussion

Characterization of prepared activated carbon

Properties of activated carbon prepared from plantain leaf sheath waste are represented in Table 2. Scanning electron microscopy is one of the most useful techniques to study the surface morphology of the prepared biosorbent (Fig. 2). It can be seen from the micrographs that the surface has well developed pores. As a result of activation process, the pores are slightly irregular and vary in size and shape.

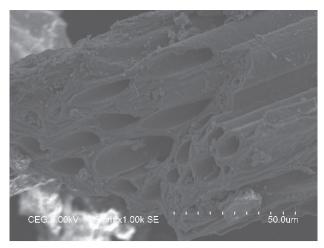


Fig. 2 – Scanning electron microscope image of activated carbon prepared from Plantain Waste

The FTIR spectra analysis of before and after dye adsorbed activated carbon is shown in Fig. 3(a,b,c). The spectra provided details about various functional groups on the surface of activated carbon. As shown in the figure, new peaks are detected in the dye adsorbed activated carbon. Significant peaks were observed at 2000–3800 cm⁻¹ belonging to O–H, C–H groups and NH stretching, and peaks at 1050–1700 cm⁻¹ belonging to C–O, C=O groups and –C=C– stretching. The bands indicate the involvement of functional groups on the surface of activated carbon in the dye adsorption process.

Adsorption studies

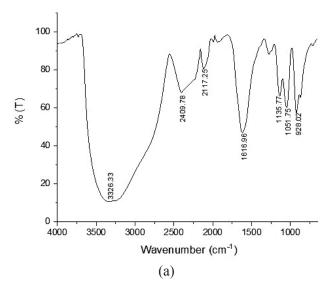
Effect of contact time

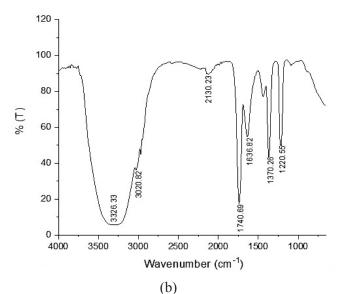
Figs. 4 and 5 show the variation of the adsorption capacity (Q_t) and percentage removal as a function of time for the dyes Reactive Green 19 and Reactive Red 141, respectively. The percentage removal and the adsorption capacity increased with the increase in contact time, and remained constant after the equilibrium time was reached.

The percentage removal and adsorption capacity of Reactive Green 19 attained a maximum value of 56.65 % and 5.75 mg g⁻¹ at an equilibrium time

Table 2 – Characteristics of activated carbon

Parameter	Value
рН	5.8±0.2
pH_{zpc}	6.7±0.2
Moisture content (%)	9.7±0.36
Ash content (%)	9.67±1.52
Volatile matter (%)	27.56±2.51
Decolourizing power (mg g ⁻¹)	13.336 ± 0.21
Iodine number (mg g ⁻¹)	198.53±6.36





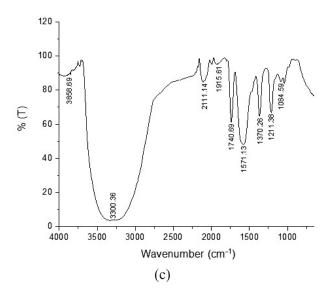


Fig. 3 – (a) FTIR spectra of activated carbon (before adsorption), (b) FTIR spectra of activated carbon (after adsorption of Reactive Green 19), (c) FTIR spectra of activated carbon (after adsorption of Reactive Red 141)

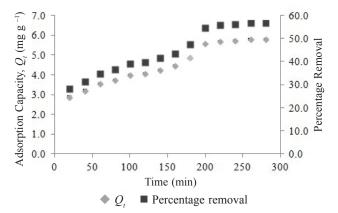


Fig. 4 – Adsorption rate curve of Reactive Green 19 (initial dye concentration = 200 mg L^{-1} ; adsorbent dosage = 1.0 g/50 mL; pH = 6)

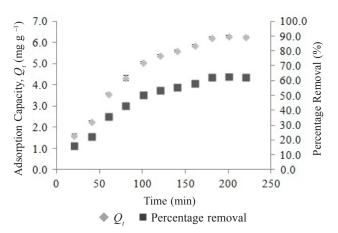


Fig. 5 – Adsorption rate curve of Reactive Red 141 (initial dye concentration = 200 mg L^{-1} ; adsorbent dosage = 1.0 g/50 mL; pH = 6)

of 220 min. Likewise, the percentage removal and adsorption capacity of Reactive Red 141 reached equilibrium at 180 min exhibiting the values of 62.72 % and 6.28 mg g⁻¹, respectively. The higher initial adsorption rate was due to the presence of large numbers of vacant adsorption sites available at the initial stage of the adsorption process. The vacant adsorption sites and high dye concentration resulted in an increased concentration gradient between the solute in solution and the solute on the adsorbent surface³⁴. The adsorption curves are smooth and leading to saturation, which indicates the possible monolayer coverage of dye on the surface of the adsorbent³⁵. As time progressed, few surface sites were available; therefore, only a very small increase in the dye removal was observed. Similar observations were reported in the literature^{1,36}.

Effect of initial dye concentration

The effect of the initial concentration of dyes was analyzed in the range of 100–500 mg L⁻¹ with

a fixed adsorbent dosage, and the results are given in Figs. 6 and 7. It was observed that percentage removal decreased correspondingly with respect to the increase in initial dye concentration, whereas the adsorption capacity increased. This might have been because, in low concentration adsorption systems, the ratio of the initial number of dye molecules to the available adsorption sites is low, and hence adsorption becomes independent of initial concentration. Increase in dye concentration contributes to the greater driving force to overcome the mass transfer resistance of dye from solution to the adsorbent. It allows more dye molecules to be adsorbed onto the adsorbent surface, thereby increasing the adsorption capacity^{37,38}.

The percentage removal decreased from 54.89% to 14.49% for Reactive Green 19 and from 77.32% to 35.09% for Reactive Red 141, respectively. On the other hand, the adsorption capacity increased from $3.19\ \text{mg}\ \text{g}^{-1}$ to $10.66\ \text{mg}\ \text{g}^{-1}$ for Reactive Green 19 adsorption, and in the case of Reactive Red 141 adsorption system, it increased from $3.84\ \text{mg}\ \text{g}^{-1}$ to $7.9\ \text{mg}\ \text{g}^{-1}$.

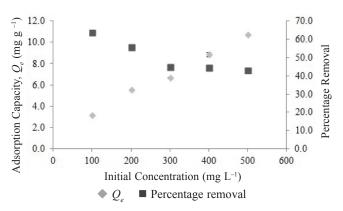


Fig. 6 – Effect of initial dye concentration on percentage removal and adsorption capacity for Reactive Green 19 adsorption (adsorbent dosage = $1.0~\rm g/50~mL$; pH = 6; contact time = $220~\rm min$)

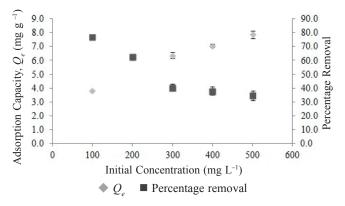


Fig. 7 – Effect of initial dye concentration on percentage removal and adsorption capacity for Reactive Red 141 adsorption (adsorbent dosage = $1.0~\rm g/50~\rm mL$; pH = 6; contact time = $180~\rm min$)

Effect of adsorbent dosage

The adsorbent dosage is a significant parameter because it determines the capacity of adsorbent for a given concentration, and also determines the sorbent–sorbate equilibrium of the system. Increase in adsorbent concentration increases the percentage removal of dyes due to the greater availability of the exchangeable sites or surface area for the adsorption¹³. On the other hand, the increase in adsorbent dosage correspondingly decreases adsorption capacity. This might be due to the saturation effect of adsorption active sites due to aggregation³⁹.

The effect of adsorbent dosage on adsorption of Reactive Green 19 and Reactive Red 141 was determined for the adsorbent dosages in the range of 0.5–2 g, and the results are given in Figs. 8 and 9. It was observed that, with increasing adsorbent dosage, the percentage removal of dyes also increased. For Reactive Green 19, the percentage removal increased from 33.43 % to 67.84 %, and in the case of Reactive Red 141, the same increased from 37.85 % to 79.87 %. The adsorption capacity

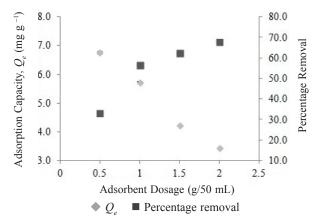


Fig. 8 – Effect of adsorbent dose on percentage removal and adsorption capacity for Reactive Green 19 adsorption (initial dye concentration = 200 mg L^{-1} ; pH = 6; contact time = 220 min)

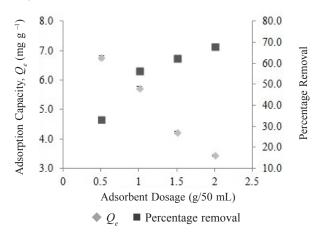


Fig. 9 – Effect of adsorbent dose on percentage removal and adsorption capacity for Reactive Red 141 adsorption (initial dye concentration = 200 mg L^{-1} ; pH = 6; contact time = 180 min)

decreased from 6.80 mg g⁻¹ to 3.45 mg g⁻¹ for Reactive Green 19 adsorption, and in the case of Reactive Red 141 adsorption system, it reduced from 7.6 mg g⁻¹ to 4.02 mg g⁻¹.

Effect of pH

The hydrogen ion concentration of a solution is an important controlling parameter in the adsorption process. The pH at zero point charge (pH $_{\rm zpc}$) is the pH at which the net surface charge on activated carbon is zero, which influences the adsorption process. For pH< pH $_{\rm zpc}$, the surface of activated carbon becomes positively charged and the dye anions are easily adsorbed on the surface by electrostatic attraction forces. On the other hand, for pH> pH $_{\rm zpc}$, the activated carbon becomes negatively charged which leads to electrostatic repulsion between adsorbent and the anionic dyes, which results in decreased adsorption⁴⁰.

The effect of pH on adsorption of reactive dyes was analyzed in the range of pH 2–12, and the results are given in Figs. 10 and 11. The pH value of

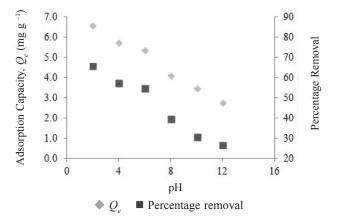


Fig. 10 – Effect of pH on percentage removal and adsorption capacity for Reactive Green 19 adsorption (initial dye concentration = 200 mg L^{-1} ; adsorbent dosage = 1.0 g/50 mL; contact time = 220 min)

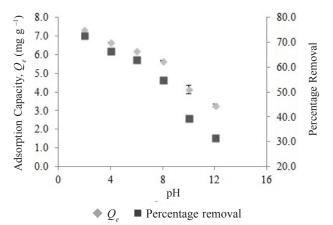


Fig. 11 – Effect of pH on percentage removal and adsorption capacity for Reactive Red 141 adsorption (initial dye concentration = 200 mg L^{-1} ; adsorbent dosage = 1.0 g/50 mL; contact time = 220 min)

Table 3 – Percentage removal of reactive dyes by adsorbents reported in the literature

S.No.	Adsorbents	Operation parameters	Adsorption efficiency	Reference
		Reactive Green 19	•	
1	Activated carbon prepared from ground nut shell (GNC)	Initial dye concentration 40 ppm Adsorbent dose 20 g L ⁻¹ Time 60 min	78.5 %	36
2	Activated carbon prepared from baby corn carbon (BCC)	Initial dye concentration 40 ppm Adsorbent dose 20 g $\rm L^{-1}$ Time 60 min	79 %	36
3	Activated carbon prepared from banana leaf sheath waste	Initial dye concentration 200 mg L ⁻¹ Adsorbent dose 1 g for 50 mL Time 200 min pH 2	65.9 %	The current study
		Reactive Red 141		
1	Activated carbon prepared from ground nut shell (GNC)	Initial dye concentration 30 ppm Adsorbent dose 20 g L ⁻¹ Time 60 min	70.7 %	36
2	Activated carbon prepared from baby corn carbon (BCC)	Initial dye concentration 30 ppm Adsorbent dose 20 g $\rm L^{-1}$ Time 60 min	75.6 %	36
3	Biochar from pecan nutshells	Adsorbent dose 0.05 g Initial dye concentration 50 mg L^{-1} Temperature 25 °C Time 4 h	86 %	48
4	Activated carbon prepared from banana leaf sheath waste	Initial dye concentration 200 mg L ⁻¹ Adsorbent dose 1 g for 50 mL Time 180 min pH 2	72.7 %	The current study

the prepared activated carbon at the point of zero charge (pH_{zpc}) was found to be 6.5. In acidic pH, the adsorption efficiency was high, and it started to decline as the pH increased. Maximum percentage removal of dyes was observed at pH 2 (65.9 % for Reactive Green 19, and 72.71 % for Reactive Red 141). Similar results have been reported in literature⁴¹. According to literature survey, the activated carbon prepared from plantain leaf sheath waste is as effective as other activated carbon (Table 3).

Adsorption isotherms

The Langmuir, Freundlich, and Temkin isotherm parameters for adsorption of Reactive Green 19 and Reactive Red 141 onto activated carbon are given in Table 4. Comparison of the R^2 values showed that the Freundlich model was applicable to describe the adsorption of Reactive Green 19 onto activated carbon. The 1/n values were within the range, indicating the favourable adsorption process.

Langmuir isotherm fitted quite well with the experimental data of Reactive Red 141 adsorption system with a high correlation coefficient of 0.995. Langmuir sorption explains that the uptake of dye

Table 4 – Adsorption isotherm constants and coefficients of determination (R²)

D			
Param	Parameters		
Reactive Green 19	Reactive Red 141		
14.9254	8.4746		
0.0049	0.0312		
0.5050	0.1382		
0.923	0.995		
2.30	1.88		
0.5220	0.2490		
0.985	0.931		
16.952	5.390		
3.4364	0.1352		
0.917	0.9319		
	Reactive Green 19 14.9254 0.0049 0.5050 0.923 2.30 0.5220 0.985 16.952 3.4364		

Table 5 – Kinetic parameters for adsorption of reactive dyes onto activated carbon

	Parameters		
	Reactive Green 19	Reactive Red 141	
Pseudo first order			
$K_1 \text{ (min}^{-1})$	0.0710	0.0238	
$Q_e (\text{mg g}^{-1})$	3.2053	11.343	
R^2	0.94	0.858	
Pseudo second order			
K ₂ (g mg ⁻¹ min ⁻¹)	0.0024	0.0011	
$Q_e (\text{mg g}^{-1})$	6.8966	9.5238	
R^2	0.955	0.975	
Intraparticle diffusion			
$K_{\rm p} \ ({\rm mg \ g^{-1} \ min^{-1/2}})$	0.2630	0.4760	
C	1.4690	0.2060	
R^2	0.947	0.952	
Elovich model			
α (g mg ⁻¹ min ⁻¹)	0.8277	2.2391	
β (g mg ⁻¹)	0.2314	5.4526	
R^2	0.9404	0.977	

occurred on a homogeneous surface by monolayer adsorption with no interaction between the adsorbed dyes⁴². Maximum monolayer adsorption capacity, $Q_{\rm max}$, was found to be 8.474 mg g⁻¹, and $R_{\rm L}$ value was greater than zero and less than unity, suggesting favourable adsorption of Reactive Red 141 onto activated carbon prepared from plantain leaf sheath waste.

Adsorption kinetics

Study of adsorption kinetics is significant as it provides knowledge about the rate of adsorption, as well as about the mechanism of adsorption. The experimental data was modelled using the pseudo-first and second-order model, intraparticle diffusion model, and Elovich model. The parameters are presented in Table 5.

For the pseudo-second-order kinetics, the correlation coefficients were found to be 0.955 and 0.975 for the dyes Reactive Green 19 and Reactive Red 141, respectively. Hence we can suggest that the adsorption system followed pseudo-second-order kinetics. Based on the observations, the rate of dye adsorption process can be controlled by the chemisorption process⁴³. The correlation coeffi-

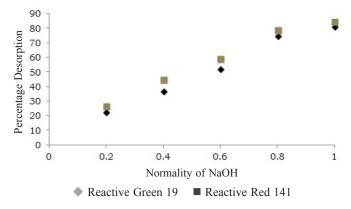


Fig. 12 – Desorption of reactive dyes from activated carbon

cients for intraparticle diffusion ($R^2 = 0.947$ for Reactive Green 19, and 0.952 for Reactive Red 141), were lower than for the pseudo-second-order kinetics. This indicated that the present system might follow intraparticle diffusion, and as mentioned previously, the plot does not pass through the origin, thus indicating that the intraparticle diffusion was not the only rate-limiting step in adsorption of reactive dyes onto activated carbon prepared from plantain leaf sheath waste.

Also, the Elovich model exhibited higher values of R^2 ($R^2 = 0.941$ for Reactive Green 19, and 0.977 for Reactive Red 141) compared with the pseudo-first-order kinetic model. This supports the fact that the adsorbent surface is energetically heterogeneous and adsorption of dyes takes place by chemisorption⁴⁴.

Desorption studies

The dye-loaded activated carbon was subjected to desorption under basic conditions. As shown in Fig. 12, the desorption efficiency improved with increasing concentration of desorbing agent. The reason for this behaviour can be explained, as follows: under strong basic (high pH) conditions, the number of negatively charged sites on the adsorbent surface increases, which in turn favours desorption of dye anions due to electrostatic repulsion⁴⁵. Hence, the desorption study guarantees the reusability of the activated carbon and the reactive dyes. The regenerated adsorbent was again subjected to adsorption, and the results showed that the adsorption efficiency had declined after the third cycle. Hence, the activated carbon prepared from plantain leaf sheath waste could be used for a maximum of three cycles.

Conclusion

In the current study, plantain leaf sheath waste has been used to produce activated carbon using phosphoric acid. Batch adsorption studies for the

removal of reactive dyes from aqueous solutions have been carried out using the prepared activated carbon. Under the optimum conditions (initial dye concentration = 200 mg L⁻¹, adsorbent dose = 1 g, pH= 2, contact time = 220 min for Reactive Green 19, and 180 min for Reactive Red 141), maximum percentage removals for Reactive Green 19 and Reactive Red 141 were obtained as 65.9 % and 72.7 %, respectively. Modelling data obtained from isotherms indicated that very good fits were produced with the Langmuir isotherm for Reactive Red 141 adsorption and Freundlich isotherm for Reactive Green 19 adsorption. Kinetics data show that the rate of adsorption is controlled by chemisorptions. Activated carbon prepared from plantain sheath waste is as effective as other adsorbents reported in the literature. According to desorption studies, the activated carbon can be reused thrice. Thus, from this study, we can conclude that activated carbon produced from chemical activation of the plantain wastes has the potential of adsorbing reactive dyes from industrial effluents.

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