

ADSORPTION PROCESS OF REACTIVE RED 2 USING A LOW-COST ACTIVATED CHARCOAL: ISOTHERM, KINETICS AND THERMODYNAMICS STUDIES

A. Anandan , T. Janakiram

Srimad Andavan Arts and Science College (Autonomous), Tiruchirappalli-05

Corresponding Author E-mail: anandan.ari@gmail.com

Abstract

Activated charcoal with an appropriate functional group was synthesized by carbonizing method, from stem of *Albizia Lebbeck*. The average 75-125 μm mesh was utilized to separate particles. The charcoal parameters of bulk density, surface area, moisture content, pH, and pH_{zpc} have been measured, which are in concurrent with literature reported values. Chemical functionality was studied by FT-IR spectroscopy and particle size was confirmed by scanning electron microscopy. The dye, Reactive Red 2 (Red2), adsorbs on the surface of activated charcoal through microscopic holes. General parameters variations, namely exposure time, adsorbent dosage, initial dye concentration, temperature, and pH of the dye solution, were used to find out a best condition for dye removal. Compare to the reported adsorbents that require acidic conditions ($\text{pH} < 5$), the prepared charcoal has been capable of absorbing Reactive Red 2 at an ambient pH of 5.5. The equilibrium adsorption data were found to match with the Langmuir and Freundlich isotherms, and thermodynamic tests indicated the endothermic adsorption process. Furthermore, it has been proven by Lagergren and models, the monolayer coverage and first-order kinetics of adsorption indicate the scalability of the adsorptive process for large-scale dye removal from waste-water streams.

Keywords: *Albizialebbeck*, Reactive red 2, activated charcoal, adsorption isotherm, Langmuir, Freundlich.

1. Introduction

Natural or synthetic colorants (dyes) are being used in most sectors, including textiles, tanneries, paints, pulp, paper etc. These dyes are having hazardous nature such as, carcinogenic, and allergenic. The dyes discharged in the effluent create significant environmental contamination.¹⁻² Eventually, humans are exposed to dye effluents, which can cause dermatitis,

cancer, jaundice, tumors, skin irritation, and heart abnormalities.³ As a result, it is necessary to remove or reduce dangerous dyes from effluents before they enter into the environment. On the other hand, treating these dyes from waste water is cumbersome because the dyes are stable organic compounds that are resistant to aerobic digestion and are light, heat, and oxidizing agents' persistent.⁴ As a result, one of the most significant challenges facing the textile industry is the removal of colour from dye-house effluents. To remove dyes from aqueous effluents, a range of methods have been investigated, including physical, chemical, and biological treatments, as well as combined approaches.^{5,6} Physical and chemical procedures such as coagulation-flocculation, adsorption, oxidation, and membrane processes are commonly employed to remove dyes due to their biodegradability.⁷ Adsorption is one of the most effective strategies for removing colors from textile wastewater.⁸

Because of its simple design (experimental setup), ease of operation, and cheaper cost, the adsorption approach is now widely utilized to remove dye pollutants from effluents. This method can also be used to extract harmful heavy metals and poisonous organic compounds.⁹

Although activated carbon is the most common and efficient adsorbent¹⁰ (Ghanizadeh et al. 2009), its commercial form cannot be employed as a desirable choice in developing nations due to high production costs and recovery.⁹ When compared to the cost of commercial activated carbon, it is well recognized that activated carbon made from biomaterials or waste materials is less expensive.¹¹ As a result, scientists have tried to make activated carbon from natural wastes such as waste wood, orange peels, coffee husks, pine cones, dairy sludge, rice husks, peanut hulls, jack fruit peels, coconut tree, bamboo grass, and so on.^{11,12}

In this study, we used the dried stem of *Albizia lebbek* as a botanical waste to make activated charcoal (ALSC), which served as the adsorbent. *Albizia lebbek* stem was chosen because of its larger availability, ease of processing, and reduced cost. The produced activated charcoal (ALSC) was utilised in batch mode studies to investigate the influence of exposure length on the elimination of reactive red 2 dye with different adsorbent doses, beginning dye concentrations, pH, adsorbent size, and temperature. We conducted various experiments to better understand the kinetics and thermodynamic parameters of the removal of reactive red 2 from

aqueous solution on the surface of activated charcoal (ALSC), and the results were used to plot various models such as Lagergren,¹³ Bhattacharya-Venkobachar,¹⁴ Langmuir¹⁵, and Freundlich¹⁶.

2. Materials and Methods

2.1 Materials

Sigma-Aldrich provided analytical quality reagents and Reactive Red 2 dye, which were used without additional purification. Scheme 1 depicts the chemical diagram of reactive red 2 dye.

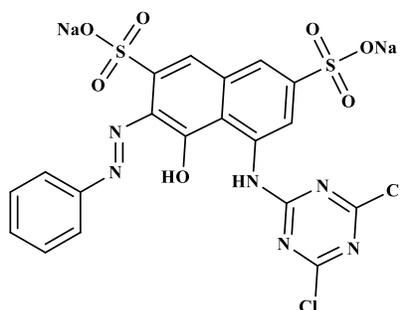


Fig. 1 Molecular structure of Reactive Red 2 dye

2.2 Experimental Methods

2.2.1 Carbonization

The synthesis of activated carbon from the plant *Albizia lebbek* involves multiple processes, including the purchase of raw materials, treatment with activating agents such as H_2SO_4 , $ZnCl_2$, or H_3PO_4 , carbonization, and activation. The plant was purchased locally, and when the bark was removed, it was sliced into little pieces and dried. Pyrolysis is the heating, decomposition, and conversion of ALSC into the required product in a fixed bed reactor in an inert atmosphere at temperatures below 800 °C. Most non-carbon elements, hydrogen, and oxygen were first eliminated in gaseous form during carbonization through pyrolytic breakdown. As a result, the carbonization process entailed the thermal degradation of carbonaceous material, the removal of non-carbon species, and the formation of a fixed carbon mass and rudimentary pore structure¹⁷. The carbonized product's quality and yield are determined by the heating rate, final temperature, and soaking period. At roughly 500 °C, the porous char's basic microstructure was developed. The tarry compounds that emerged during pyrolysis were discovered to seal some of these pores, which were only freed up after a further heat treatment at around 800 °C. Further heat treatment

at temperatures above 1000 °C usually resulted in the carbon structure hardening due to partial alignment of the graphitic planes and a decrease in porosity, which slowed the activation.

2.2.2. Chemical Activation

The purpose of activation was to improve the porosity and enlarge the size of the pores created during the carbonization process, resulting in the production of a well-developed and easily accessible pore structure with a large interior surface area. The wood was impregnated with a concentrated solution of activating agents¹⁸ as H₂SO₄ and CaCl₂ and pyrolyzed between 400 and 600 °C in the absence of air for the chemical activation (calcination) process. Charring and aromatization occurred after calcination of impregnated and chemically dehydrated raw material, resulting in the formation of porous structures. Both activating agents (H₂SO₄ and CaCl₂) were dehydrating agents¹⁸, influencing pyrolytic breakdown and inhibiting the generation of tar, acetic acid, methanol, and other compounds while increasing carbon output. The pyrolyzed product was then cooled and filtered to remove the activating agent, which was then recycled.

2.2.3. Acid Process

By treating ALSC with concentrated sulphuric acid or phosphoric acid at 120-130 °C, a pseudo-activated carbon was created. The material began to char very immediately, accompanied by the release of heat and smells. After the reaction had died down, the mixture was placed in an air oven for 24 hours at 120-130 °C. The product was washed with excess water to remove free acid, then dried at 110°C for 30 minutes before being thermally activated at 800°C. The activated ALSC was pulverized in a mortar and pestle and sieved using American Standard Testing Mesh into numerous size fractions. The sieved particles were then dried overnight at 110°C in a hot air oven. Desiccators were used to chill the particles after they were removed from the oven. They were then placed in airtight containers for further analysis.

2.3 Characterization of activated charcoal

The surface area, pore size, and particle size of activated charcoal are well known to be key characteristics in understanding their adsorption process. As a result, we conducted the following

characterization investigation to better understand their surface properties and the adsorption mechanism of the activated charcoal we prepared (ALSC).

2.3.1. Surface Area, Pore Size Distribution and Particle Size Analysis

The BET method was used to estimate the surface area of activated charcoal (ALSC) using nitrogen as the adsorbate at liquid nitrogen temperature. To measure the quality of activated charcoal, the pore-specific volume was also determined in sorptomatic. Particles were sieved using the American Standard Testing Mesh (ASTM), and those with a mesh size of 75-125 were chosen for further testing.

2.3.2. FT-IR Spectra and SEM Analysis

A Perkin-Elmer FT-IR spectrophotometer was used to evaluate the activated charcoal that had been manufactured. Scanning Electron Microscope was used to examine the surface morphologies of activated charcoal.

2.3.3. Bulk Density and the Moisture Content

A trip balance was used to fill the activated charcoal in the 50 mL graduated cylinder to determine the apparent density of activated charcoal (ALSC). Before filling a 50 mL graduated cylinder with activated charcoal, it was carefully weighed. With constant tapping, a sufficient amount of activated charcoal was transferred and filled to the 50 mL mark. The balance's shaker was adjusted such that the charcoal filled the graduated cylinder at a rate of roughly 1 mL per second. The charcoal was correctly weighed when it was put into the graduated cylinder. By dividing the weight of charcoal by 50, the bulk density was obtained. A Petri dish containing around 5.0 g of activated charcoal (ALSC) was weighed to assess the moisture level. For around 4 hours, the meal was baked in an air oven at 105 ± 5 °C. The dish was covered and weighed after cooling in a desiccator. At 30-minute intervals, the heating, chilling, and weighing were repeated until the difference between the two successive weighing was less than 5.0 mg.

$$\text{Moisture content (percent by mass)} = \frac{100 (M-X)}{M}$$

where 'M' is mass in grams of the material taken for test and 'X' is mass in grams of the material after drying.

2.3.4. Loss on Ignition

The ASTM C311 technique was used to determine the activated charcoal (ALSC) loss on ignition. To eliminate the moisture, weighed activated charcoal was dried to a consistent weight in an oven at 105-110 °C. The ingredients were then fired to constant mass in an exposed porcelain crucible in a muffle furnace at a regulated temperature (750 50 °C). The percentage of loss on ignition was calculated after a minimum of 15 minutes of heating.

$$\text{Loss on ignition(\%)} = \frac{A}{B} \times 10$$

Where, 'A' is a loss in mass between 105 and 750 °C, 'B' is the mass of the moisture-free sample.

2.3.5. Matter Soluble in Acid and water

To test the solubility of activated charcoal (ALSC) in acid, 5 g of the material was weighed and placed to a 1 L beaker, along with 300 mL of 0.25 N HCl. The liquid was brought to a boil for around 5 minutes while being constantly stirred. After that, the mixture was allowed to settle, and the supernatant liquid was filtered through an asbestos-matted Gooch crucible. The method was carried out three times with the residue in the beaker, each time using 300 mL of acid. In a volumetric flask, the combined filtrate was concentrated to less than 100 mL after the fourth treatment. On a water bath, exactly 50 mL of the concentration was transferred to a china dish and evaporated to dryness. Finally, the residue was dried in an electric oven set to 105°C. The dish was then covered and weighed after cooling in a desiccator. The drying, cooling, and weighing method was repeated every 30 minutes until the difference between two consecutive weighing was less than 5.0 mg.

$$\text{Matter soluble in acid (\%)} = \frac{(M_1 \times 100 \times 2)}{M(100 - X)/100}$$

where M is the mass of the residue in grams, M₁ is the mass of the material taken for test in gram and X is the percentage of moisture in the material.

The same approach as before was used to determine the solubility of activated charcoal (ALSC) in water. The sole variation is that instead of 300 mL of 0.25 N HCl, 300 mL of water is used.

2.3.6. pH and Zero point charge

Weighing 10 g of dried activated charcoal and transferring it to a 1 L beaker 300 mL of newly boiled and cooled water (adjusted to pH 7.0) was added to the pot and brought to a boil. The solution was filtered while hot after being digested for 10 minutes, with the first 20 mL of the filtrate being rejected. The pH of the leftover filtrate was evaluated using a pH metre after it was cooled to room temperature. Using the pH drift method, the pH at the potential of zero charges of carbon (pH_{zpc}) was determined. 0.1M sodium hydroxide or hydrochloric acid was used to alter the pH of the solution. To remove the dissolved carbon dioxide, nitrogen was bubbled through the solution at 25 degrees Celsius. The activated charcoal was added to 50 mL of the solution at a 50 mg/mL ratio. The ultimate pH was measured after stabilization. The activated carbon's zero point charge was calculated using a graph of final pH vs beginning pH.

2.4 Preparation of Solutions

2.4.1 Stock Reactive Red Dye solutions

The dye stock solution was made by dissolving 1.0 g of reactive red 2 [disodium 5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-4-hydroxy-3-(phenylazo)naphthalene-2,7-disulpho-nate; M.F: $C_{19}H_{10}Cl_2N_6Na_2O_7S_2$; M.W: 615.33 g/mol] in With established initial concentrations, the stock solutions were diluted. The maximum wavelength of reactive red 2 was measured to be 540nm. The 0.25 g of 1,5-diphenyl carbazide was dissolved in 100 mL of 50% acetone, and the 11.0 mL of concentrated sulphuric acid was diluted to 100 mL with double distilled water.

2.4.2 Measurement of solution pH

The pH of the stock solution of reactive red 2 was adjusted to around 5.5-6.0 by pipetting in dil. NaOH (0.1M) solution. In a bottle, a known volume of the solution (50 mL) was added to 2.0 g of activated charcoal (ALSC). The bottle was stored in a motorized water bath shaker with a thermostat (Remi). The bottle was taken out of the shaker after 15 minutes and the adsorbents were separated using Whatman 40 filter paper. A pH metre (Digital pH metre model LT 120, Elico) was used to determine the pH of the filtrate, which was then reported as solution pH.

2.5 Experimental Set-Up for the Study of Adsorption Kinetics and Adsorption Equilibria

Adsorption kinetics and equilibria were investigated using batch-mode adsorption. The 2.0 g of activated charcoal (ALSC) was carefully weighed and mixed with 50 mL of reactive red 2 solutions with a specified concentration (50 mg/L) at pH 5.0–6.0 for adsorption kinetics. To guarantee equal mixing, the speed of agitation was kept constant throughout the experiment, and a temperature-controlled mechanical water bath shaker was used. All of the operations were carried out at the same temperature. The adsorbents were separated by filtering after a set period of time, and the filtrate was tested to determine the residual dye content. Experiments were repeated to see if the size of the adsorbent particles, the dose of the adsorbent, the pH of the adsorbate, and the temperature of the solution had any effect on the rate and mechanism of adsorption.

The 2.0 g of activated charcoal (ALSC) was carefully weighed and placed in a stoppered vial to evaluate the adsorption equilibria. It was pipetted 50 mL of reactive red 2 solutions with a defined concentration (50 mg/L) into it. The solution's pH was determined and recorded. The bottle was kept in a motorized shaker with a temperature control. To achieve consistent mixing, the agitation speed was kept constant. According to previous research, the contact duration required to achieve equilibrium is 3 hours¹⁹. The bottle was taken from the shaker and placed in a water bath at room temperature for roughly half an hour after attaining equilibrium. The filtrate was submitted to dye estimation colorimetrically using an ELICO colorimeter after the activated charcoal was separated by filtration. Similar experiments were carried out with varied initial concentrations of reactive red 2 dye solutions (50, 100, 150, 200, 250, 300, 400, and 500 mg/L) to see if the Langmuir and Freundlich isotherms could be applied to the current system. The tests were repeated to see how the pH of the solution affected the Langmuir constants and Freundlich parameters. After separating the adsorbent, the pH of the clear solution was tested at the end of the experiment, and it was discovered that there was little variation between the initial and final pH values. The experiments were repeated twice unless otherwise specified, and the mean value of each set of experiments was reported.

3. Results and Discussion

3.1 Characterization of the activated charcoal (ALSC)

The use of activated charcoal in wastewater treatment is mostly owing to the vast capacity of the adsorption process to remove pollutants. As previously stated, high surface area, low hardness or abrasion resistance, and moisture content are all desired features for activated charcoal for a successful adsorption process. Bulk density, pH of solutions, impurity leaching from activated charcoal, and activated charcoal solubility in water and acid are also essential characteristics. Furthermore, the ash content is another measure that provides information on the inorganic elements found in activated charcoal. Because the amount of particular inorganic constituents varies from one grade of carbon (activated charcoal) to the next, owing to the fact that they are generated primarily from the source material or activated agents used during its preparation²⁰. The adsorption process' ability to remove pollutants from wastewater may be influenced by the variables listed above. We had classified the *Albizia lebeck's* prepared activated charcoal (ALSC) as agricultural waste in this case.

The bulk density of the prepared activated charcoal is 0.3867g/cc, the moisture content is 1.76 percent, and other parameters, such as loss on ignition 84 percent, acid insoluble matter 2.43 percent, water-soluble matter 0.76 percent, pH 6.6, pH_{zpc} 5.65, and surface area 324.5m²/g, are all positive, according to the results. These parameters are similar to those found in activated charcoal made from the *Azadirachta Indica* plant in a previous study¹⁹. Furthermore, the features of the powdered activated charcoal created from *Albizia lebeck* in this study fall within the range of characteristics parameter of other activated charcoals prepared from various agricultural wastes²¹. The active charcoal has a low quantity of moisture, ash, and volatile compounds, indicating that the particle density of this charcoal is relatively low, and it should be a good raw material for adsorbents used in column or fixed-bed reactors for wastewater treatment^{22,23}. Based on the literature and our experimental results, manufactured activated charcoal appears to have a low moisture content and a smaller particle density in our study, and it is employed as an adsorbent to remove reactive red 2. FT-IR and SEM examination are also used to better understand the surface of activated charcoal, and the results are given below.

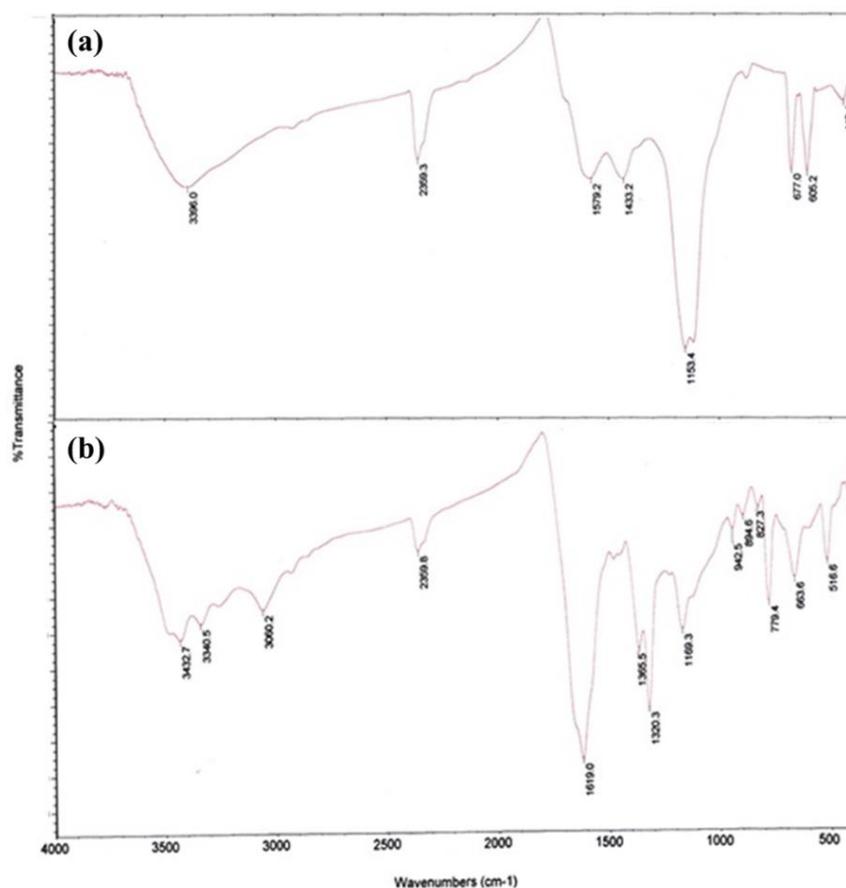


Fig. 1 FT-IR Spectrum of (a) Raw ALSC and (b) ALSC after Reactive Red 2 Adsorption

3.2 FT-IR spectra of raw activated charcoal and reactive red 2 loaded charcoal

The functional groups found on the surface of activated charcoal were examined using the FT-IR technique, which could be responsible for dye adsorption. The raw activated charcoal and reactive red 2 loaded charcoal FT-IR spectra were recorded before and after the adsorption procedure, as shown in Fig. 1. (a, b). The vibrational bands appear at 3396, 2359, 1579, 1433, and 1153 cm^{-1} , respectively, due to the existence of OH, C=O, C=C, and COC stretching vibrations, as illustrated in fig. 1 (a). The vibrational frequency of the O–H bond is modified to 3433 cm^{-1} is may be after reactive red 2 adsorptions over the surface of activated charcoal. Similarly, the vibrational frequencies of C=C and CO have shifted to 1619 and 1169 cm^{-1} , respectively, which could be attributed to reactive red 2 adsorption on the surface of activated charcoal. It should be observed that in the reactive red 2 loaded charcoal (Fig. 1 b), several new

peaks appeared at 3340, 3060, 1366, and 1320 cm^{-1} , which are attributable to NH, aromatic CH, symmetrical and asymmetric S=O in the SO_3Na group in the reactive red 2 molecule. The difference between free-loaded activated charcoal and reactive red 2 loaded activated charcoal is evidence of physical forces adsorbing dye on the adsorbent^{24,25}.

3.3 Scanning electron microscope

Figure 2a and b illustrate the surface morphology of reactive red 2 loaded activated charcoal after the dye adsorption method. The surface of unloaded activated charcoal was rough and even, as seen in Fig.2a. There was a considerable pore structure with rough small cavities. The pores were discovered to have a diameter of 10 to 25 micrometres. The surface of the pore structure has tiny holes, which are indicated in Fig. 2 a. Briefly, SEM pictures of free-loaded activated charcoal revealed that it has a rough surface with an almost non-compact structure, as well as a large number of pore spaces and microscopic cavities, where the reactive red 2 dyes can be trapped and adsorbed into the tiny cavities under the right conditions. The microscopic voids have darkened after treatment with dye (Fig. 2b), indicating that dye has adsorbed on the surface of the carbon via physisorption²⁴⁻²⁶. The SEM pictures in Fig. 2b show that the dye can be homogeneously adsorbed on the adsorbent's surface, and their surfaces are discovered to be not very random but rough in order to adhere the solute species to the adsorbent's surface. The adsorptive qualities of activated charcoal are projected to be highly effective, based on the FT-IR and SEM investigation.

In SEM pictures of activated charcoal, an array of hollow cylindrical pores may be seen. The interconnecting necks and kinks linking the cylindrical holes are clearly visible on the fracture surfaces in Fig. 2 a. SEM is a common method for determining pore morphology, and activated charcoal with cylindrical holes has been shown to have intriguing adsorptive properties²⁷.

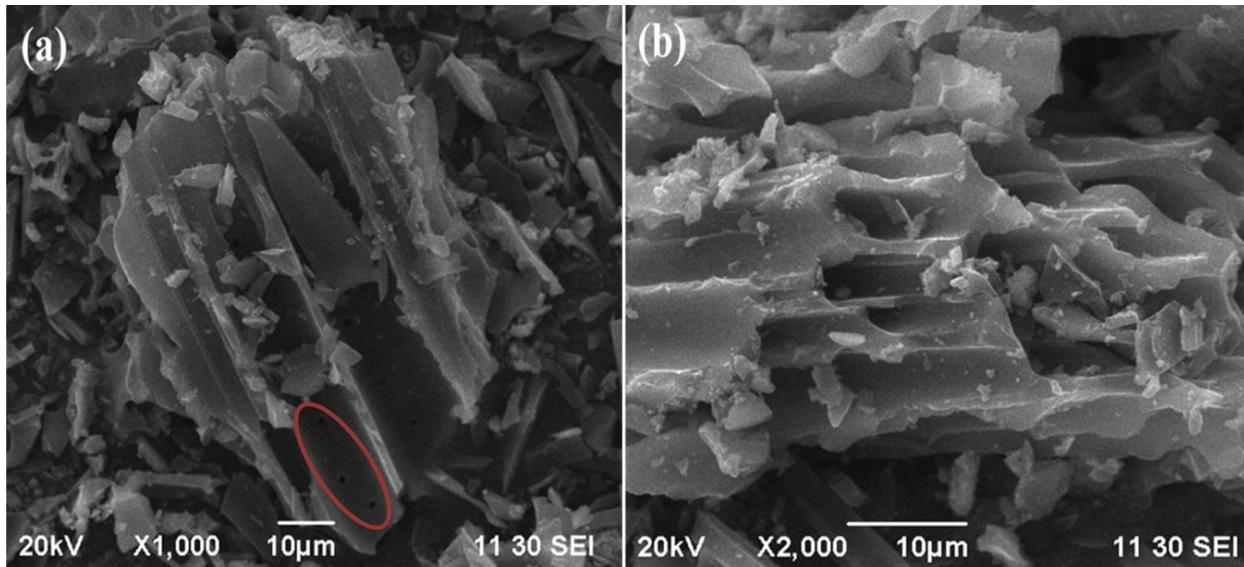


Fig. 2 SEM Image of (a) free-loaded activated charcoal and (b) reactive red 2 loaded charcoal.

3.4 Effect of contact time, the dosage of adsorbent and initial concentration of dye

We conducted numerous batch tests with varying contact periods (30-210 min), amounts of adsorbent (2.0-10.0 g/L), and dye concentrations (50-250 mg/L) to determine the ideal conditions for the adsorption process²⁸⁻³⁰. Table 1 summarizes the findings, and fig. 3 depicts the corresponding graphs (a-c). We conducted studies with a variety of contact times, including 30, 60, 90, 120, 150, 180, and 210 minutes, with a minimal amount of activated charcoal (2.0 g/L) and a dye concentration of 50 mg/L, to determine the ideal contact time^{31,32}. The minimum amount of dye adsorbed corresponding to the equilibration period was found to be 48.4 percent at the least contact time, according to the findings (30 min). The largest amount of dye adsorbed (69.2%) with contact times of 180 and 210 minutes, on the other hand. It should be noted that the dye adsorption on the surface of activated charcoal is saturated after 180 minutes of contact time, as shown in fig. 3a. We conducted trials with different dosages of the adsorbent, namely 2, 4, 6, 8, and 10 g/L, to determine the optimal doses of the adsorbent for the removal of reactive red 2. The results showed that as the dosage of the adsorbent is increased, the elimination of reactive red 2 increases²⁸⁻³⁰ as shown in fig. 3b. We also conduct trials with several concentrations, such as 50, 100, 150, 200, and 250 mg/L, to determine the best concentration³³. The % elimination of

reactive red 2 reduces as the concentration of the solution increases³³, according to the results (fig. 3-c and Table -1).

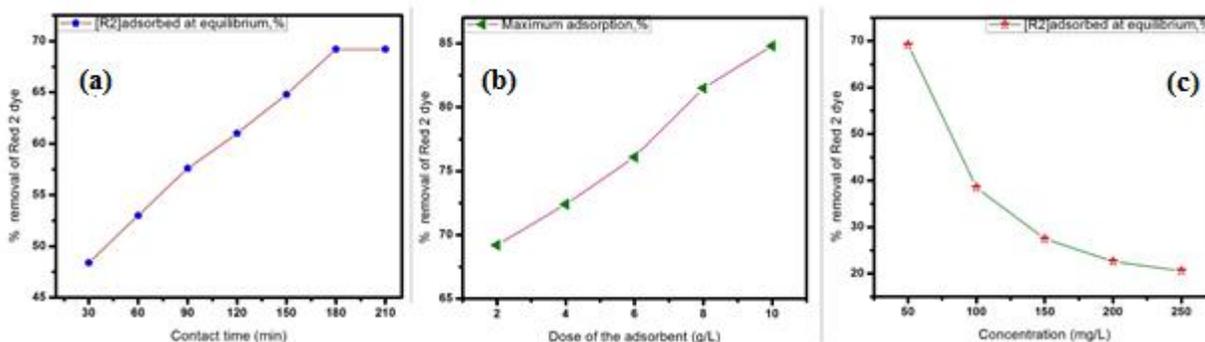


Fig. 3(a)Effect on the removal of reactive red 2 on activated charcoal (a) contact time; (b) dose of the adsorbent; (c) initial concentration of dye.

Table-1 Effect of Contact Time, Dose of the Adsorbent and Concentration on the Removal Red of Reactive 2

S. No.	Effect of contact time		Effect of dose of the adsorbent		Effect of the concentration	
	Contact time, min	[R2]adsorbed at equilibrium,%	Dose of the adsorbent m, g/ L	Maximum adsorption,%	Concentration of R2, mg/L	[R2]adsorbed at equilibrium,%
1	30	48.4	2.0	69.2	50	69.2
2	60	53	4.0	72.4	100	38.5
3	90	57.6	6.0	76.1	150	27.46
4	120	61	8.0	81.5	200	22.6
5	150	64.8	10.0	84.8	250	20.6
6	180	69.2				
7	210	69.2				

3.6 Effect of pH, size of the adsorbent and temperature

We conduct numerous tests with different pH's to determine the effect of pH³⁴⁻³⁷ on the adsorption of reactive red 2 dye onto activated charcoal (1-8). Table 2 and Fig. 4a summarizes the findings. The adsorption of the reactive red in the strong acidic medium was found to be in the range of 50.0-58.4%, according to the findings. The adsorption rate increases as the acidity of the medium decreases. The pH: 6.0 of the medium was determined to have the highest adsorption (69.0 percent). Adsorption, on the other hand, diminishes as the pH of the medium rises (7.0-8.0). The ideal pH for successful removal of reactive red 2 from the effluent is determined to be about 5.0-6.0, as shown in Figure 4a. This research suggests that a less acidic or neutral media is better for adsorption. This research has a bright future because the adsorption procedure does not necessitate the use of a strong acid or basic.

We conducted studies with different sizes of adsorbent³⁸ (75-125, 125-200, 200-250, 250-300) to determine the optimum particle size for the efficient removal of reactive red. The experimental results of reactive red 2 adsorptions onto activated charcoal with various adsorbent sizes are described in Table-2a and presented in Fig. 4b. The highest adsorption (69.2%) was attained in particles ranging in size from 75 to 125, and this is attributed to the increased surface area of the adsorbent. The surface area of the adsorbent, on the other hand, diminishes as particle size increases. As a result, the adsorption process slows down as the adsorbent particle size grows larger.

The influence of temperature on the adsorption of reactive red 2 has also been investigated, and the results are shown in Tables 2a and fig.4c. It is generally known that when the temperature rises, the adsorption process accelerates³⁹⁻⁴². In this investigation, a similar pattern was discovered. The adsorption increases as the temperature of the medium rises (35 -50 °C) (69.2 -77.1 percent). Adsorption is more advantageous at higher temperatures³¹⁻³⁴, as shown in Fig. 4c, and is found to be an endothermic process.

3.7 Adsorption Kinetics

Adsorption kinetic studies are crucial in the treatment of aqueous effluents because they reveal critical details about the adsorption process' mechanism. The experimental data for the

adsorption of reactive red 2 onto the surface of the adsorbent under the given set of conditions were analyzed in the light of Lagergren's¹¹ pseudo-first-order model, which is presented in Table-3, in order to determine the mechanistic parameters associated with the adsorption process. For the plot of $\log_{10} (q_e - q)$ against time, t , the Lagergren¹¹ equation supports linearity. The relationship between $\log_{10} (q_e - q)$ and t under a certain set of experimental conditions is depicted in Fig.-5a. The rate constants were calculated using the slope of each line. Table-5 shows the $k_{\text{Bhatt}} \times 10^4 \text{s}^{-1}$ values obtained at pH 5.5 using varied concentrations of the adsorbent. Bhattacharya and Venkobachar equation¹² validated the results obtained in light of Lagergren, and the values are reported in Table 4. The k_{Bhatt} values are found to be similar to the k_{Lager} values. These figures demonstrate a declining tendency when the adsorbent dosage is increased⁴³ (Fig. 6). The Bhattacharya and Venkobachar equation¹² further validates the production of a monomolecular layer of reactive red 2 dye on the adsorbent surface, as well as the first-order kinetic nature of the process shown in Fig.5b.

Table -2 Effect of pH on removal of reactive red 2 dye

S. No.	Effect of pH	
	pH	[R2] _{adsorbed} at equilibrium, %
1	1.0	50.0
2	2.0	53.8
3	3.0	58.4
4	4.0	63.2
5	5.0	67.1
6	6.0	69.0
7	7.0	67.2
8	8.0	58.2

Table -2a Effect of size of the adsorbent and temperature on removal of reactive red 2 dye

Effect of Pore Size of the Adsorbent		Effect of Temperature	
Average Pore Size of the adsorbent (μm)	[R2] _{adsorbed} at equilibrium, %	Temperature °C	[R2] _{adsorbed} at equilibrium, %
75-125	69.2	35	69.2
125-200	65.4	40	72.8
200-250	60.1	45	74.9
250-300	56.5	50	77.1

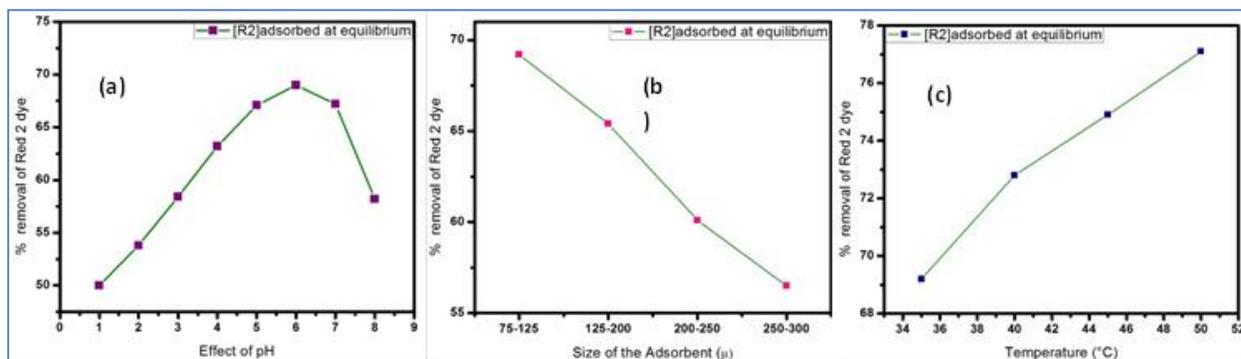


Fig. 4(a)Effect on the removal of reactive red 2 on activated charcoal (a) pH; (b) particle size; (c) temperature.

Table -3 Effect of contact time on reactive red 2 removal – concentration variation

S. No.	Contact time t, min	$2+\log_{10}(q_e-q)$				
		Initial Conc.(mg/L)				
		50	100	150	200	250
1	30	2.7160	2.7032	2.6989	2.6901	2.7118
2	60	2.6074	2.6180	2.5682	2.6020	2.6074
3	90	2.4623	2.4698	2.4842	2.4548	2.4698
4	120	2.31175	2.3010	2.2671	2.2430	2.3010
5	150	2.04139	1.9030	2.02118	1.8129	2.0791

Table -4 Effect of contact time on reactive red 2 removal–concentration variations

S. No.	Contact time t, min	2+log(1-U _t)				
		Initial Conc. (mg/L)				
		50	100	150	200	250
1	30	1.4779	1.4189	1.3851	1.3360	1.3010
2	60	1.3694	1.3336	1.2543	1.2479	1.1966
3	90	1.2243	1.1855	1.1704	1.1007	1.0590
4	120	1.0737	1.0166	0.9533	0.8889	0.8902
5	150	0.8033	0.6186	0.7073	0.45880	0.6684

Table -5 Effect of the concentration of the solution on k_{Lager} and k_{Bhatt}

S. No.	[R2] _{ini.} , mg/L	k _{Lager} X 10 ⁴ , s ⁻¹	k _{Bhatt} X 10 ⁴ , s ⁻¹
1	50	2.11	2.11
2	100	2.45	2.11
3	150	2.11	2.11
4	200	2.68	2.68
5	250	1.99	1.99

Table -6 Data for Langmuir and Freundlich plot

S. No.	[R2] _{ini.} , C ₀ , mg/L	x, mg / L	C _e , mg / L	log C _e	(x/m), q _{e.} , mg/g	log q _e	C _e /q _e
1	50	34.6	15.4	1.1875	17.3	1.2380	0.8901
2	100	38.5	16.5	1.7888	19.25	1.2844	3.1948
3	150	41.2	108.8	2.0366	20.65	1.3149	5.2687
4	200	45.2	154.9	2.1900	22.6	1.3541	6.8539
5	250	51.5	198.5	2.2977	25.75	1.4107	7.7087

Table -7 Isotherm Constants for Adsorption of Reactive Red 2 on ALSC

Langmuir Isotherm Constants			Freundlich Isotherm Constants		
Q _m (mg/g)	b (L/mg)	Correlation Coefficient (R ²)	K _F (mg/g)	n (L/mg)	Correlation Coefficient (R ²)
26.525	0.0525	0.9765	0.0568	7.526	0.8525

Table -8 Values of R_L for Reactive Red 2 Adsorption on ALSC

S. No	[R2] _{ini.} , C ₀ (mg/L)	R _L
		Temp., 35 °C
1	50	0.2757
2	100	0.1599
3	150	0.1126
4	200	0.0869
5	250	0.0707

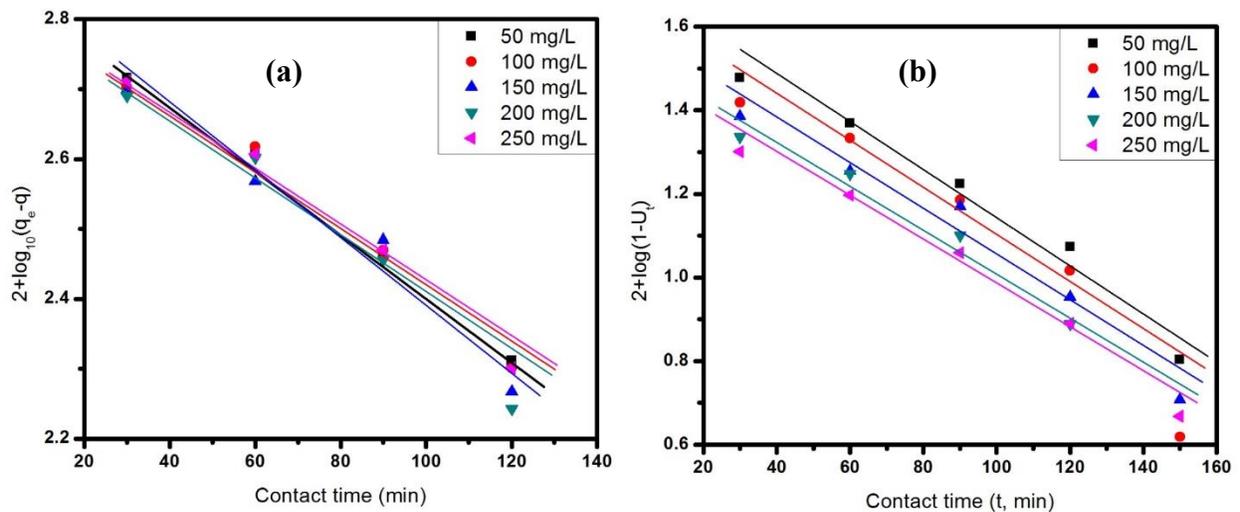


Fig. 5 The plot-concentration variation: (a) Lagergren and (b) Bhattacharya-Venkobachar

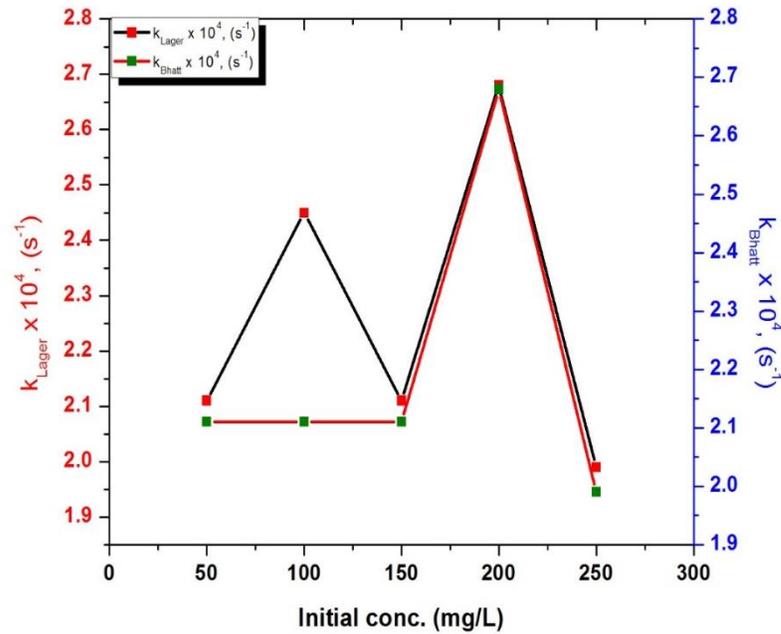


Fig. 6 Effect of the concentration of the solution on $k_{Lagergren}$ and $k_{Bhattacharya}$ -concentration variation

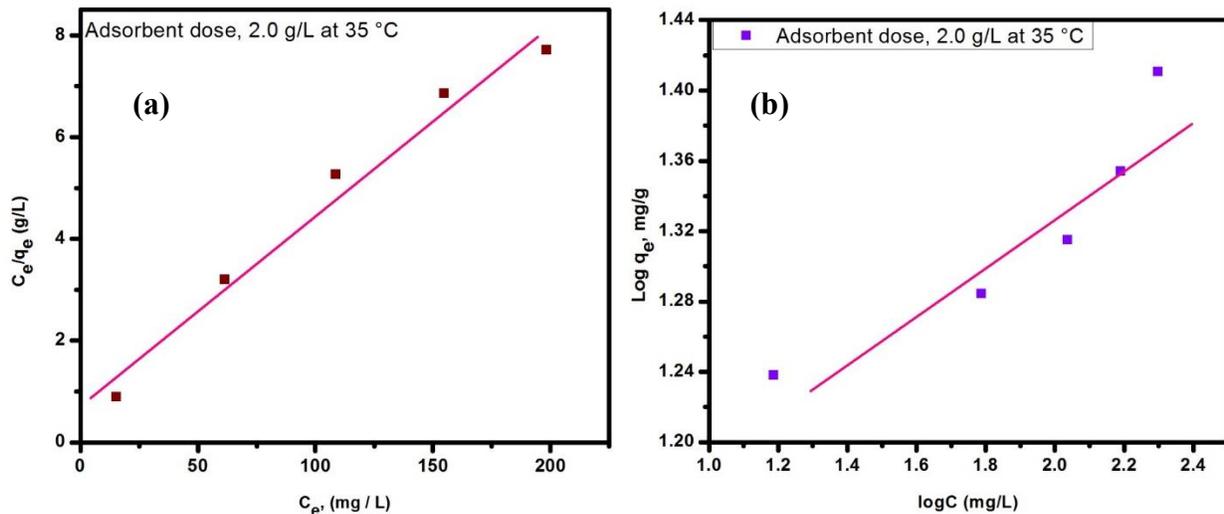


Fig. 7 (a) Langmuir isotherm; (b) Freundlich isotherm

3.8 Adsorption Isotherms

A linear variant of the Langmuir¹⁵ and Freundlich¹⁶ isotherms was used to examine the experimental data. Table-6 displays the results. The linear plots of C_e/q_e versus C_e demonstrate

that the Langmuir isotherm depicted in Fig.7 is applicable (a). The slope and intercepts of the plots were used to calculate the values of Q_m and b , which are provided in Table-7. The adsorption of reactive red 2 follows the Freundlich isotherm (Fig.7 (b)), as shown by the linear plot of $\log q_e$ versus $\log C_e$ in Fig.7 (a). Table-7 lists the K_F and n values that were discovered. The R_L values of activated charcoal in Table-8 and Fig. 8 indicate that the adsorption process is favorable^{43,44}.

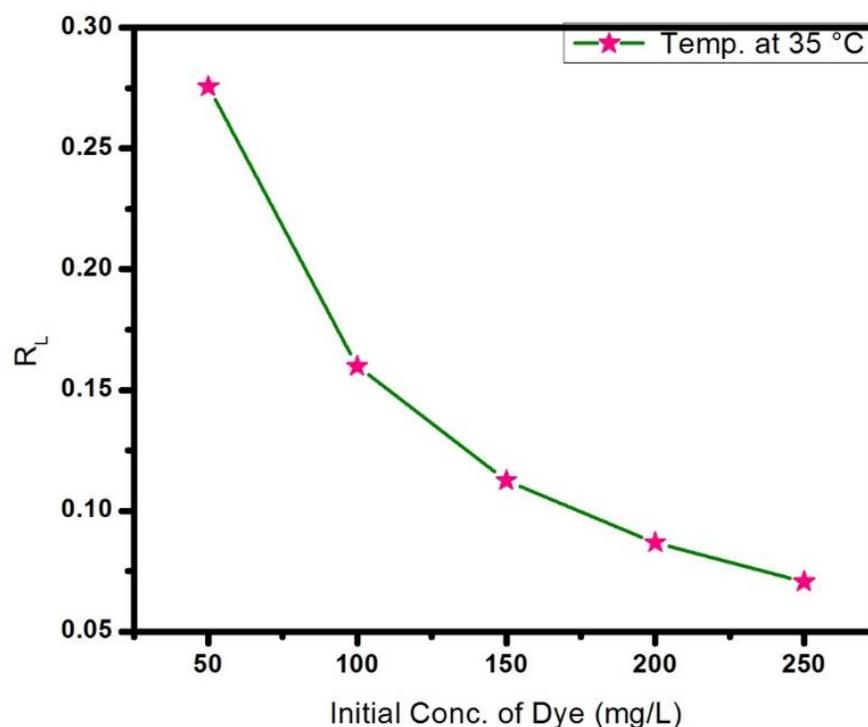


Fig. 8 Values of R_L for Reactive Red 2 adsorption on activated charcoal

4. Conclusion

The activated charcoal was made from agricultural waste Albizia lebeck using carbonization and chemical activation method. For this study, activated charcoal particles with a mesh of 75-125 μm were chosen. The bulk density (0.3867g/cc) and moisture content (1.76%), loss on ignition (84%), acid insoluble matter (2.43%), water-soluble matter (0.76%), pH (6.6), pHzpc (5.65), and surface area (324.5 m^2/g) are comparable to other activated charcoals which are derived from other agricultural waste. The prepared bulk density (0.3867g/cc) and moisture

content (1.76 percent) are both lower than previously reported bulk density (0.3867g/cc) and moisture content (1.76 percent). SEM study of loaded and free-loaded activated charcoal revealed that the adsorptive character of activated charcoal is high and effective, based on the previous characteristics parameter and FT-IR.

The percent removal of reactive red 2 increases with increasing adsorbent dose and decreases with increasing adsorbate solution concentration in the current study. Similarly, as the adsorbent dose is increased, the minimum time required to achieve maximum adsorption increases. The pH level that should be fixed for future experiments is 5.5. The Lagergren and Bhattacharya-Venkobachar models' applicability indicates the creation of a monomolecular layer of reactive red 2 species on active charcoal's surface. It also demonstrates the adsorption process's first-order kinetic character. Langmuir and Freundlich isotherms were found to be well represented by the equilibrium data, and thermodynamic tests confirmed the endothermic nature of the adsorption process. The R_L values have proven the adsorption process's favorability. All of the foregoing data suggests that the chosen ALSC could be employed as an adsorbent to remove reactive red 2 from wastewaters.

Conflicts of interests Statement

The Authors declares that there is no conflict of interest.

Data availability statement

The authors declare that all the data supporting the findings of this study are available within the article.

References

- [1]. Robinson, T (2001). Remediation of Dyes in Textile Effluent: A Critical Review on Current Treatment Technologies with a Proposed Alternative. *Bioresour. Tech.*, 77 (3), 247- 255.
- [2]. Huang, R (2017). Adsorption of methyl orange onto protonated cross-linked chitosan. *Arabian Journal of Chemistry*, 10(1), 24–32.
- [3]. Alver, E (2012). Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies, *Chem. Eng. J.* 200: 59–67.

- [4]. Sun, Q. (2003). The adsorption of basic dyes from aqueous solution on modified peat-resin particle, *Water Res.*, 37 (7), 1535-1544.
- [5]. Ghaneiyan, M (2009). Use egg shells as a natural adsorbent for the removal of reactive red 123 dye of textile wastewater. *J Tabib Shargh*.11:25-34.
- [6]. Naimabadi, A (2009). Decolorization and Biological Degradation of Azo Dye Reactive Red2 by Anaerobic/Aerobic Sequential Process, *Iran. J. Environ. Health. Sci. Eng.*, 6 (2), 67-72.
- [7]. Kafil, Z (2011). Study of dye removal from aqueous solution using sawdust and clay. *Modares civil engineering J*.11:67-76.
- [8]. Pajoohehfar, S.P (2009). Adsorptive removal of phenol from contaminated water and wastewater by activated carbon, almond, and walnut shells charcoal. *J. Water Environ Res.* 81, 641-648.
- [9]. Hadi, M (2010). Model to evaluate dye removal from aqueous solutions in fixed-bed columns of activated carbon *J. water and waste water*, 1:23-34.
- [10]. Ghanizadeh, G.H (2009). Removal of methylene blue dye from synthetic wastewater with bone char, *J environment and health*, 2:104-113.
- [11]. Aseel M. Aljeboree (2007). Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon, *Arab. J. Chem.* 10, S3381-S3393.
- [12]. Kaur, S (2013). Adsorption Kinetics for the Removal of Hazardous Dye Congo Red by Biowaste Materials as Adsorbents. *J. Chem.*, 2013, 1–12.
- [13]. Lagergren, S (1898). “Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, *Kungliga Svenska Vetenskapsakademiens*,” *Handlingar*, 24 (4), 1-39.
- [14]. Bhattacharya, A. K (1984). Removal of Cadmium (II) by Low Cost Adsorbents. *J. Environ. Engg.* 110(1), 110.
- [15]. Langmuir, I (1918). The Adsorption of Gases on Plane Surfaces of Glass, Mica And Platinum *J. Amer. Chem. Soc.* 40, 1361-1403.
- [16]. Freundlich, H. Adsorption in Solution. *Zeitschrift für Physikalische Chemie*, 57, 384-470.

- [17]. Derbyshier, F (1995). Porosity in carbons: characterization and applications, Editor: Patrick, J.W., Edward Arnold Pub., London, 227p.
- [18]. Bansal R.C (1988). Active Carbon, Dekker Pub., New York.
- [19]. Anandan, A (2021). Studies on the Adsorption of Cr (VI) from Aqueous Solution by Low Cost Activated Carbon J Adv. Sci. Res. 12 (2) 323.
- [20]. Soleimani, M (2007). Agricultural Waste Conversion to Activated Carbon by Chemical Activation with Phosphoric Acid, Chem. Eng. Technol, 30 (5), 649.
- [21]. Madu, P.C (2013). Physicochemical characteristics of activated charcoal derived from melon seed husk J. Chem. Pharm. Res., 5(5), 94.
- [22]. Ekpete, O A (2011). Sorption kinetic study on the removal of phenol using fluted pumpkin and commercial activated carbon Int. J. Biol. Chem. Sci. 5(3):1143–1152.
- [23]. Ekpete, O.A (2011). Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (*Telfairiaoccidentalis* Hook F) Res. J ChemSci 1(3):10–17.
- [24]. Arivoli, S (2007). Kinetic and thermodynamic studies on the adsorption of some metal ions and dyes onto low cost activated carbons, Ph. D., Thesis, Gandhigram Rural University, Gandhigram.
- [25]. Almasi, A (2016). Walnut shell as a natural adsorbent for the removal of Reactive Red 2 form aqueous solution, Intl. Res. J. Appl. Basic. Sci. 10 (5), 551-556.
- [26]. Weber, W.J (1967). Principle and Application of Water Chemistry, edited by Faust, S.D., and Hunter, J. V., Wiley, New York.
- [27]. Osei-Wusu A (2012). A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope, Scanning Electron Microscopy,
- [28]. Selvarani, K (2000). Studies on Low-cost Adsorbents for the removal of organic and Inorganics from Water, Ph.D., Thesis, Regional Engineering College, Thiruchirappalli.
- [29]. Jia, Y.F (2002). Adsorption of Metal Ion on Nitrogen Surface Functional Groups in Activated Carbon, Langmuir, 18, 470.
- [30]. ThillaiNatarajan, S (2011). The removal of heavy metal chromium (VI) from aqueous solution by using marine algae *Graciliriaedulis*. J. Chem. Pharm. Res., 3(2), 595-604.

- [31]. Namasivayam, C (1996). Removal of dyes from aqueous solutions by cellulosic waste orange peel. *Biores. Technol.*, 57, 37-43.
- [32]. Namasivayam, C (1995). Adsorption of direct red 12 B by biogas residual slurry: Equilibrium and rate processes *Environ. Pollut.* 89, 1-7.
- [33]. Manjunath, D.L. and Mehrotra, I.: Removal of reactive dyes using alum, lignin sludge. *Indian J. Environ. Health*, 23: 309-315 (1981).
- [34]. Ghosh, D (2002). Adsorption of methylene blue on kaolinite, *Appl. Clay Sci.* 20, 295-300.
- [35]. Vadivelan, V (2005). Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interf. Sci.*, 286, 90-100.
- [36]. Guo, Y (2005). Use of Rice Husk-Based Porous Carbon for Adsorption of Rhodamine B from Aqueous Solutions, *Dyes and Pigments*, 66, 123.
- [37]. Sreedhar, M.K (1999). Mercury (II) adsorption of desorption characteristics of coconut husk based carbon- Kinetics and self-diffusion, *Indian J. Environ. Protect.* 19, 8.
- [38]. Sekaran, G (1995). Adsorption of dyes by buffing dust of leather industry, *Indian J. Chem. Technol.*, 2, 311.
- [39]. Saseetharan, M.K (1985). Dye house waste colour removal-Adsorption studies. M.E. Thesis. Govt. College of technology. Bharathiar University. Coimbatore.
- [40]. Periasamy, K (1991). Studies on Chromium (VI) Removal by Activated Ground nut Husk Carbon, *Indian J. Environ. Hlth.*, 33, 433.
- [41]. Rajachandrasekar, T (2006). Cobalt Adsorption on a Low Cost Carbon–Kinetic, Equilibrium and Mechanistic Studies, *Mat. Sci. Res. India*, 3, 241-250.
- [42]. Hema, M (2007). Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon, *Intern. J. Phys. Sci.*, 2, 10-17.
- [43]. Moore J. W (1984). Heavy metals in natural water: Applied Monitoring and Impact Assessment. Springer-Verlag: New York.
- [44]. Sudha, R (2007). Comparative study on the adsorption kinetics and thermodynamics of metal ions onto acid activated low cost pandanus carbon. *E-J. Chem.*, 4, 238-254.