

Valorization of *Annona reticulata* biochar by chitosan for the adsorption of Azo dye from Textile effluent

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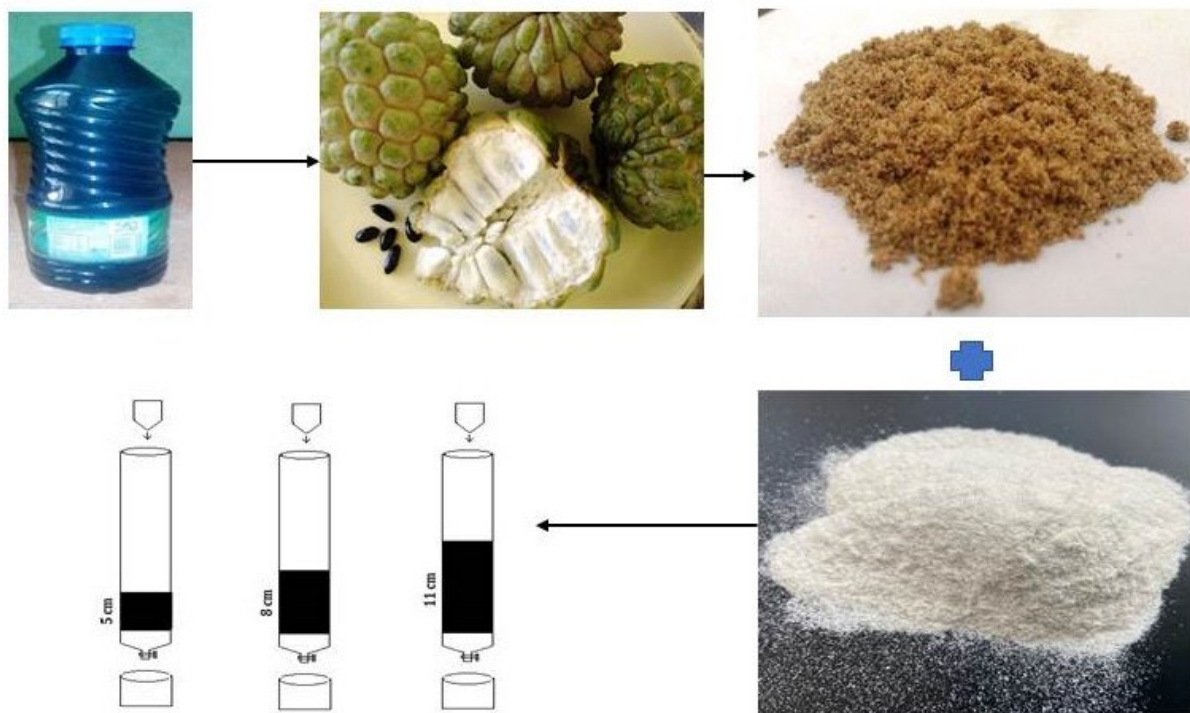
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GRAPHICAL ABSTRACT



Abstract

Azo dye is a synthetic aromatic dye which are direct dye frequently used in textile industry to colour fibres. It also contributes to the damage of the environment. This study examines the adsorption biochar made from *Annona reticulata* to remove azo dye from textile wastewater. To improve the adsorption capacity, biochar valorized by chitosan molecules, Investigations were conducted on the use of chitosan-based materials that are acid-resistant for azo dye adsorption. In the batch experiment, basic operating parameters such as initial Azo dye concentrations, pH, contact time and bed height were assessed. The percentage removal efficiency for Azo dye was recorded as 67.18%, 75.88% and 94.37% for three dissimilar sized columns that were 6cm, 8cm, and 10cm. The UV–visible absorption spectroscopy was used to quantify the decolorization of dyes. The changed surface properties of the adsorbent produced from *Annona reticulata* were characterized by using SEM, XRD, and FTIR. The effectiveness of the column's adsorption was calculated mathematically by Yoon-Nelson, Thomas, and Adams-Bohart models. The model that best represents equilibrium isotherm data by adsorption had R^2 values of 94.63, 86.67 and 96.35 respectively.

Keywords: Azo dye removal, Textile wastewater, *Annona reticulata*, Chitosan, Adsorption.

1. Introduction

The textile industry is one of the major contributors to serious pollution issues around the world because it is a significant industrial consumer of water and a significant producer of wastewater [1]. The increased demand for textile products has also led to an increase in the generation of textile wastewater [2]. The classification of textile industries is based on the kinds of fabrics they create, such as cellulosic materials derived from plants, protein fabrics derived from animals, and synthetic fabrics created artificially [3]. In textile factories, both dry and wet techniques are used to produce fiber. The wet procedure releases highly contaminated wastewater while using a sizable amount of potable water [4]. This procedure includes techniques for sourcing, sizing, de-sizing, bleaching, mercerizing, dyeing, printing, and finishing. The discharged colored effluents are a significant non-aesthetic pollution source, and the oxidation, hydrolysis, or other chemical reactions that occur during the wastewater phase result in hazardous by-products that are released into the environment [5]. The textile industry's primary environmental harm comes from the discharge of untreated effluents into water bodies, which typically account for 80% of all emissions produced by this sector [6]. Biochemical oxygen demand (BOD) and Chemical oxygen demand (COD) are

relatively high levels in most residual fluids from the textile industry [7]. The abundance of non-biodegradable chemical substances, particularly textile colors, should receive more attention [8]. Azo dye molecules are harmful to higher living organisms, including aquatic environments and plants, since they are toxic, carcinogenic, teratogenic, and mutagenic. Approximately 15-20% of azo dyes are discharged as wastewater into aquatic habitats because they are not anchored to the substrate [9]. A serious threat to aquatic life and indirectly to human health is posed by the presence of minute amounts of azo dyes, which are quite apparent and have a negative impact on the clarity and quality of water bodies like lakes, ponds, and rivers [10]. Bladder cancer in humans has been connected to azo dye ingredients like benzidine. Moreover, azo dye exposure increases the risk of bladder cancer in dye workers [11]. Therefore, azo dyes are genotoxic, mutagenic, carcinogenic, and have deadly consequences on both people and animals. The reckless release of azo dyes into the environment, especially from the textile industry, is of great concern to both human health and the environment [12]. One of the unit activities in the chemical engineering procedures used to treat the wastewater from the textile industry is adsorption [13]. Due to the ease of the procedure and reduced cost compared to other processes, adsorption is a well-established technology for azo dye removal from wastewater [14]. The technique becomes even more economically efficient when adsorbents made from different biomass wastes, such as biochar and activated carbon, are developed [15]. For the treatment of dye wastewater, biochar has been found as a possible contender. Due to the presence of surface functional groups and the biochar's substantial surface area, it is advantageous to employ biochar for wastewater treatment [16]. Several studies have investigated the environmentally beneficial usage of biochar for the removal of colour from textile effluent in the past [17]. The purpose of this study was to investigate how effectively azo dye might be removed from treated textile effluent [18]. Batch adsorption process was proceeded for the removal of azo dye and UV-visible absorption spectroscopy was used to quantify the decolorization of dyes [19]. SEM, XRD, and FTIR characterisation techniques provided strong support for the experiment. The mathematical modelling Yoon-Nelson, Thomas, and Adams-Bohart models were reinforced the adsorption process [20]. Intraparticle diffusion model and repeated studies of the adsorbent's regeneration capacity was conducted.

2. Martials and Methods

2.1. Preparation of column material

The *Annona reticulata* seed was collected, dried completely for 10 hours at 100°C in a hot air oven, and then manually broken into numerous pieces [21]. The microbiological particles were fully crushed out after that, and the column material was collected and cleaned with a NaCl solution [22]. Again, it was allowed to dry for 10 hours in a hot air oven set to 100°C and for 5 hours in the open air.

2.2. The adsorbent surface activation by chitosan particles

100 mL of a 0.1M acetic acid solution were used to dissolve 0.5 g of chitosan to create the basic chitosan solution [23]. The dissolution process took place at room temperature for 3 hours with constant stirring, after which the solution was left to stand for 10 hours [24]. Sulfate anions were used as crosslinking bridges to create chitosan nanoparticles. By combining a solution of chitosan with a solution of $K_2SO_4 \cdot 7H_2O$ at a constant concentration in a volume ratio of 1:1 while stirring [25], chitosan sulfate aqueous dispersions were created. Chitosan was present in the combinations at a constant concentration of 2 gL^{-1} [26]. SEM surface examination of a superficially modified adsorbent.

2.3. Column study

The particle sizes ranging from 0.8 mm to 3 mm of adsorbent was prepared and it was filled in column and the bottom was covered with class glass wool [27]. The three different sized 6cm, 8cm and 10cm filled adsorbent column with the flow rate of 3 ml/min was used for the adsorption study [28]. The column study conducted in the room temperature, In the fixed bed column studies, a glass column with an inner diameter of 3 cm and a length of 80 cm was used [29].

2.4. Spectrophotometric analysis

HCl or NaOH solutions were used to modify the pH of the solution. In each experiment, which was carried out twice [30], The UV-visible spectrophotometer method was used to determine the amount of dye in the solutions. With the following expression, the amount of dye adsorbed per unit mass of resin was determined:

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

Where C_o and C_e (mg/L) were the preliminary and symmetry dye concentrations in the aqueous solution, and the adsorbent capacity, q_e (mg/g) [31]; The experimental solution's volume, V (ml), and adsorbent's weight, m (g), were both given.

2.5 Kinetic study

2.5.1 Thomas Model

The Thomas model was used to calculate the relationship between solute concentration and time [32]. In continuous column technology, both internal and external mass transfer restrictions were considered.

$$\ln\left(\frac{C_o}{C_t} - 1\right) = (K_t * q * m/Q) - k_t * C_o * t$$

where m is the mass of the adsorbent, C_o and C_t are the influent and effluent concentrations (mg/L), K_t is the Thomas rate constant (mL/(min.mg)), and t is the duration (min), Assuming a constant flow rate, the volume of adsorbent in the column was restrained as Q (g), and the adsorption kinetics (k_t) were determined from the plot of $\ln [(C_o/C_t)]$ over time [33].

2.5.2 Adams-Bohart model

Construction of fixed bed columns most usually employs the Adams Bohart. This model was developed with the presumption that the adsorbate is quickly adsorbed onto the adsorbent surface, and that intra-particle diffusion and external mass transfer resistance are unimportant factors [34]. The first 10 to 50% of the saturation points, or the breakpoint, of the breakthrough curve, are identified using this model.

$$\ln\left(\frac{C_t}{C_o}\right) = K_{ab} C_o t - K_{ab} N_{ab} \left(\frac{z}{u}\right)$$

The kinetic constant in this equation is represented by k_{ab} (L/mg min), the linear flow velocity is denoted by u (cm/min), and the saturation concentration is designated by N_{ab} (mg/L) [35]. The parameter values for k_{ab} and N_{ab} were obtained by plotting the function $\ln(C_t/C_o)$ versus t and calculating its slope and intercept. The kinetic constant k_{ab} changed as the inlet flow rate and initial dye concentration increased and decreased, respectively [36]. N_{ab} 's value increased with increasing starting concentrations. In the start of the adsorption process, external diffusion can be the reason for this. The statistic that some data did not appropriate the model precisely confirmed its errors.

2.6 Characterization of adsorbent

2.6.1. SEM Analysis

Adsorption images were captured using the SEM analytical technique. Using geometrical information from two-dimensional photos, the estimation of flocculation and aperture properties of surface area was carried out utilizing image dispensation software [37]. Examining was done using scanning electron microscopes (SEM), specifically an APE-60 syrmaks R-560 SEM equipped with 800 EDS spectrometer and an HDP-EDS detector, in order to confirm the deposited sludge during the flocculation process [38]. The execution of all extent on elegant segments was made possible by acerbating the samples and rasping the saturated segments [39]. To assess any compositional adjustment based on the intricate array of different capabilities present within the cohort of the analytical signals [40]. For the experiments to generate data that was at least passably illustrative, 800x magnification was used. This resembles squares about 1 mm² in size [41]. In both configurations, the analyses were carried out by searching four areas for each taster.

2.6.2. XRD Analysis

Azo dye removal in aqueous solution as determined by adsorption research. Highest expected dense resolution for the main Azo dye constituents, as shown by XRD [42]. Using a tube driven by X-ray diffraction, measurements of the overall concentration of the major and minor components in the adsorption were made (XRD) [43]. The operational parameters of the Topins X-ray apparatus model SNLH0 were 0 kV and with 6000 seconds were spent irradiating [44]. A Si (Li) detector was used to create the X-ray spectra, which were then analysed using the reiterative smallest quadrangular accurate computer code. IFEA standard orientation material analyses were finished as part of the measurement quality control process [45]. The stream cell contains an adsorbent sample with electrochemical responses and diffraction patterns that have been recorded [46]. The in situ electrochemical dimension that the arrangement supports is its key strength. The deflection patterns are made possible by the moving brine [47]. Since it took that long to complete the security checks and depart the experimental hutch, the XRD measurements began 6–10 minutes after the flow began through the cell.

2.6.3. FTIR Analysis

Using a Spectrum Two-Perkin Elmer Model, Fourier transform infrared spectroscopy (FTIR) was used to see the actual clusters in molecular structures at ambient temperature. The IR

spectra were used to monitor the actual assembly [48]. The vibration of the band at 640 cm^{-1} is associated with (AlCl). Due to different surroundings, (Al-O's) vibration appeared in two distinct frequencies (Al-O) [49]. As a result, the peak at 1536 cm^{-1} is like the NaCl bond expanding. Stretching and bending of the bands seen at 1742 cm^{-1} and 2610 cm^{-1} are attributed to (OH). The vibration of the band at 4254 cm^{-1} is (Al-OH) [50]. These allotted objects make up the adsorbent stages [51]. As they provide a variety of important information, the characteristic peaks of the amide groups band in FTIR are helpful for analyzing the structure of the deposited sludge [52]. The FTIR spectra of various temperature-treated adsorbents were displayed. 60 minutes were spent treating the samples at various temperatures [53]. From discs containing adsorbent-deposited sludge samples, FTIR spectra were obtained [54]. Using an infrared spectrophotometer, the spectra were measured from 6000 to 600 cm^{-1} at a data acquisition rate of 6 cm^{-1} per point.

2.6.4. Study on intraparticle diffusion

It was done using the Weber-Morris intraparticle diffusion model [55]. The subsequent equation assisted as the primer to this study:

$$q_t = K_{id}t^{0.5} + C$$

K_{id} is the rate constant of the intraparticle diffusion model, and C is a constant (mgr/gr). The linear relationship between the values of q_t and t is 0.5 can be used to derive the values of K_{id} and C .

2.7. Regeneration of adsorbent

By electrically heating the adsorbent to 400°C in both an inert and an environment with air, thermal regeneration was accomplished [56]. The adsorbent was heated to 400°C to 600°C in a muffle furnace during the hot water extraction process, twice washed with DI water and HCL solution, and then dried for an additional three hours in a hot air oven [57]. The effectiveness of the regenerated adsorbent's regeneration was determined by evaluating the azo dye removal capacity.

3. Result and Discussion

3.1. Adsorption study

Azo dye was primarily existing in effluent at a meditation of 270 mg/L . Batch process research performed to examine Azo dye adsorption in order to evaluate how well Annona

reticulata - chitosan assisted as an adsorbent for the elimination of Azo dye [58]. In order to gauge how well the treatment was functioning, samples were obtained every 10 minutes and analyzed using a UV-visible spectrophotometer technique. Studies on the initial investigation using *Annona reticulata*-chitosan columns were done [59]. Although the input trial level was 3 mL/min in a 6 cm stake, the output ranges were 1.6 mL/min. According to Table.1 & Figure.1, In 80 minutes, the column was totally drained at 88.6 mg/l for 6 cm..

Table.1 Azo dye removal for 6cm column

Time (min)	6cm column (mg/L)
0	270.0
10	213.4
20	198.7
30	175.6
40	167.5
50	133.9
60	116.3
70	108.7
80	88.6
90	88.6

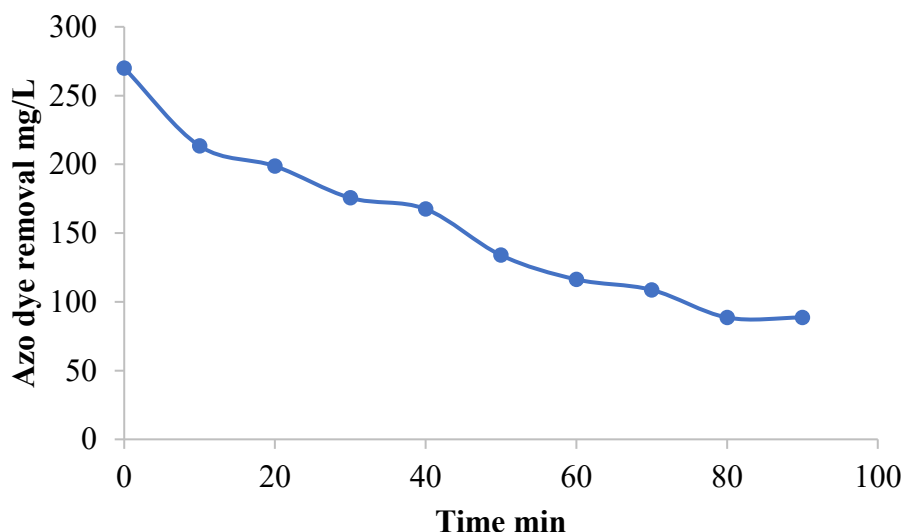


Figure.1 Azo dye removal for 6cm column

The elimination percentage in the initial adsorption study reached about 67.40%. On the second round of the study, investigations were done using *Annona reticulata*-chitosan columns [60]. The output ranges were 1.2 mL/min, while the input sample flow rate of 3

mL/min in an 8 cm column was kept constant [61]. According to Table.2 and Figure.2, Within 110 minutes, the column was entirely drained at 65.1 mg/l for 8 cm.

Table.2 Azo dye removal for 8cm column

Time (min)	8cm column (mg/L)
0	270.0
10	258.3
20	192.6
30	185.3
40	177.9
50	153.5
60	133.7
70	118.9
80	90.5
90	85.6
100	78.3
110	65.1
120	65.1

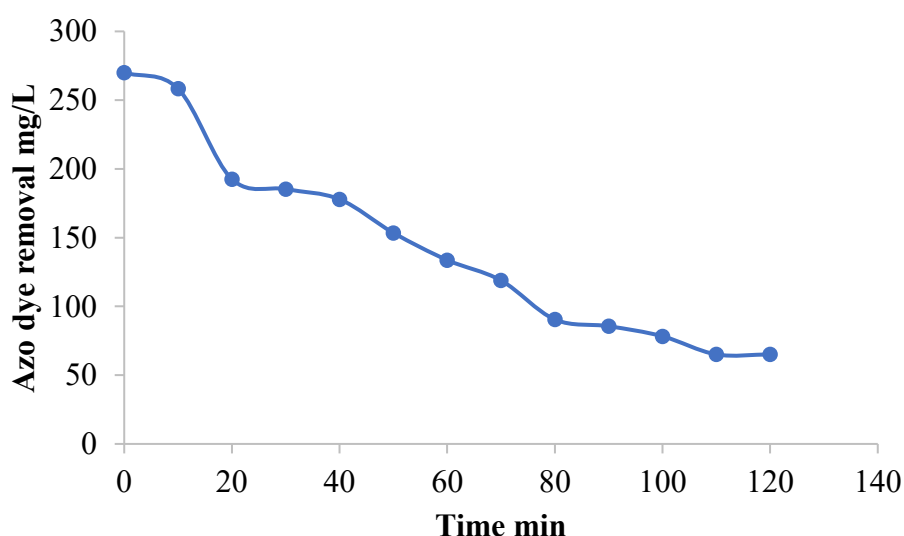


Figure.2 Azo dye removal for 8cm column

The elimination percentage reached about 75.88% in the second round of the adsorption investigation [62]. Studies were done employing *Annona reticulata*-chitosan columns during the third round of the investigation. The output ranges were 1 mL/min, while the input sample flow rate was maintained at 3 mL/min in a 10 cm column [63]. According to Table.3 and Figure.3, the column was completely depleted at a rate of 15.2 mg/l for 10 cm in 120 minutes, with a removal percentage of 94.37%.

Table.3 Azo dye removal for 10cm column

Time (min)	10cm column (mg/L)
0	270.0
10	218.5
20	164.8
30	127.6
40	103.5
50	92.4
60	76.5
70	54.2
80	38.7
90	27.9
100	16.5
110	15.8
120	15.2
130	15.2

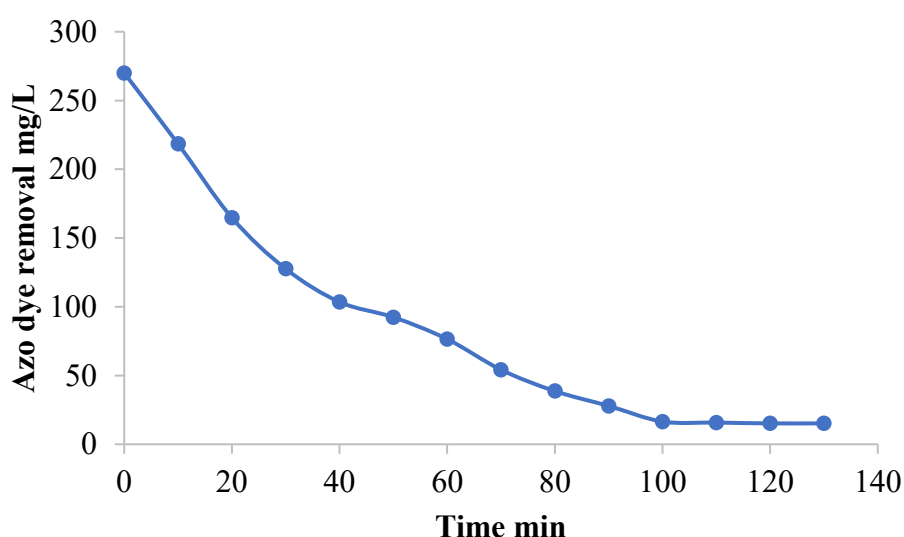


Figure.3 Azo dye removal for 10cm column

In the extensive column experiment, the initial azo dye concentration in the effluent was 270 mg/L. Using batch process study, it was feasible to assess how successfully *Annona reticulata* - chitosan removed Azo dye when used as an adsorbent [64]. The output ranges for the three different sized columns 6,8, and 10 cm differ according to the height of the bed. For the 6cm column, the output ranges were 1.6 mL/min, for the 8cm column, 1.2 mL/min, and for the 10cm column, 1 mL/min, due the height of bed the infiltration ranges vary [65]. To gauge how much of the azo dye had been removed from the sample, a UV-visible spectrophotometer was employed. In this study, the removal range for a 6 cm column was

88.6 mg/L, and after 80 minutes, the adsorption column reached saturation with a removal percentage of roughly 67.40%. The azo dye removal range in the following investigation for an 8 cm column was 65.1 mg/L in 110 min, and the adsorption column was saturated with a removal percentage of roughly 75.88%. The end experiment had a height of 10 cm, a removal range of 15.2mg/L in 120 minutes, and a removal percentage of 94.37% [66]. This study demonstrated how the elimination of azo dye is influenced by the contact time, flow velocity, and column depth. The size of the column was determined at 6 cm, 8 cm, and 10 cm based on the thorough study. The column separates the azo dye from the wastewater because of its infiltration capability [67]. This experiment used a surface-modified adsorbent to regulate the ideal azo dye concentration in the textile effluent.

3.2. Kinetic study

3.2.1. Adsorption experiment analysed by Thomson model

The ionic speciation of the adsorbate laid in the required region controlled the adsorption process. It was assessed using the Thomas model [68]. The measured and predicted breakthrough curve for the adsorption process agreed, as evidenced by the maximum regression coefficient value (R^2) for a 10 cm column, which was 0.972. The greatest concentration of adsorbate had favorable adsorption kinetics, as evidenced by the mass (m) and time of concentration effect kt 's value (t) [69]. Kt values initially minor, and in subsequent stage it increased as 0.027, 0.024, and 0.029 for the column. Temperature increase caused a decrease in the rate constant (kt). The equilibrium uptake capacity slightly increased (q_0). The decrease in q_0 showed that, as the chart plainly states, the adsorption capacity is negatively associated with bed height and contact time.

Table.4 Adsorption experiment analysed by Thomson model

Material	Column size (cm)	$k_t \times 10^{-3}$ (mL/(min.mg))	q_0 (mg/g)	R^2
Annona reticulata - Chitosan	6	0.027	6.52	0.901
	8	0.024	3.40	0.936
	10	0.029	6.86	0.972

3.2.2. Adams-Bohart model

The 60% of the saturation points of the breakthrough curve are described by this model. The kinetic constant K_{ab} varied as the initial adsorbent concentration, bed height, and inflow flow

rate did, in that order [70]. Nab's value is developed at higher original solvent concentrations. This may have occurred at the beginning of the electro adsorption process due to diffusion from the outside. Table 5 exhibits the standard for R^2 , K_{ab} , and N_{ab} . As not all values fit into the model, it had limits.

Table.5 Adams-Bohart model for Three different study

Material	Column size (cm)	N_{ab} (mg/L)	K_{ab} (ml/mg min)	R^2
Annona reticulata - Chitosan	6	146.10	0.0017	0.913
	8	137.41	0.0028	0.948
	10	187.22	0.0032	0.975

3.3. Characterisation study

3.3.1. SEM Analysis

SEM pictures were used to describe the microstructures and morphologies of Annona reticulata - Chitosan. Figure 6 illustrates how the dark-colored structural modifications and abundant asymmetrical shacks in azo dye result in more lively adsorption sites. [71]. A closer look at the structure revealed that it had retained its black color long after magnetization. With a diameter of about 350 nm, the crystal domains are consistently ornamented and decisively attached to the adsorbent surface in accordance with the magnetic microspheres created adsorbent surface changes [72]. As shown in figure.4 with varying sizes presenting a block-like structure and smooth surface, for compelling separation, a homogeneous distribution of magnetite on the adsorbent's external is beneficial.



Figure.4 SEM analysis of *Annona reticulata* – Chitosan adsorbent

3.3.2. XRD Analysis

Figure 6 displays the XRD patterns of the *Annona reticulata*-Chitosan adsorbent. The diffraction pattern of the adsorbent lacks a glassy peak, indicating an amorphous structure for the azo dye adsorption [73]. Figure 6 illustrates how XRD reveals the distinctive peaks of an adsorbent at 40.5° (250), 36.3° (352), 42.5° (280), 58.7° (613), and 69.5° (540). The outcomes imply that the introduction of the magnetic adsorbent into the adsorption study was successful. Also, unlike the XRD patterns of azo dye removal, no carbon peak was seen for the adsorbent, showing that it still has an amorphous structure following hydrothermal magnetization [74]. They exhibit a type I isotherm now, which suggests that they are mesoporous. This is added reinforced by its minute hysteresis rings in the relative pressure P/P_0 region between 0.2 and 0.6. According to their pore structure properties, azo dye has a lower surface area and pore volume (2653 m^2 and 1.53 cm^3 , respectively) while adsorbing than adsorbent (3261 m^2 and 1.84 cm^3 , respectively). Because mutually high and low external area carbonaceous elements are used to create the magnetic composite, the exact adsorbent's superficial area was decreased.

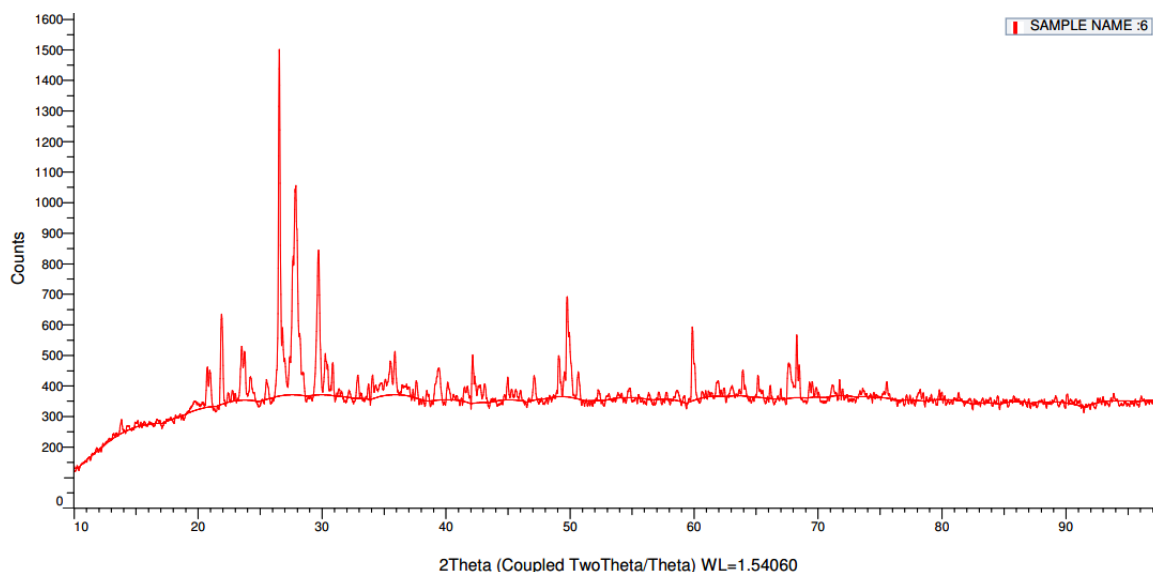


Figure.5 XRD analysis of Annona reticulata – Chitosan adsorbent

3.3.3. FTIR Analysis

Figure 7 shows the FTIR spectrum of the Annona reticulata-Chitosan adsorbent. There are some adsorbed azo dyes and coordinated water present at the same time, as shown by the faint absorption peaks at 3421 and 453.27 /cm, which pertain to the circuitous trembling and stretching vibration of the OH- bond. [75]. In the case of an adsorbent, A peak at 2883.58 cm was found by XRD examination, and it may be associated to the flexural vibration of C-H, as well as bands at 2831.50 cm and 2385.95 cm that were ascribed to the O-H distortion trembling and the C=C extending quivering [76]. The large absorption maxima at 1633.71 cm and 727.16 cm of Annona reticulata-Chitosan adsorbent are attributed to the carboxyl groups' (-C=O-) and C-H bending vibrations. C-O stretching and O-H bending (in-plane) vibrations are responsible for the broad band that may be seen between 1043.49 and 775.38 cm.

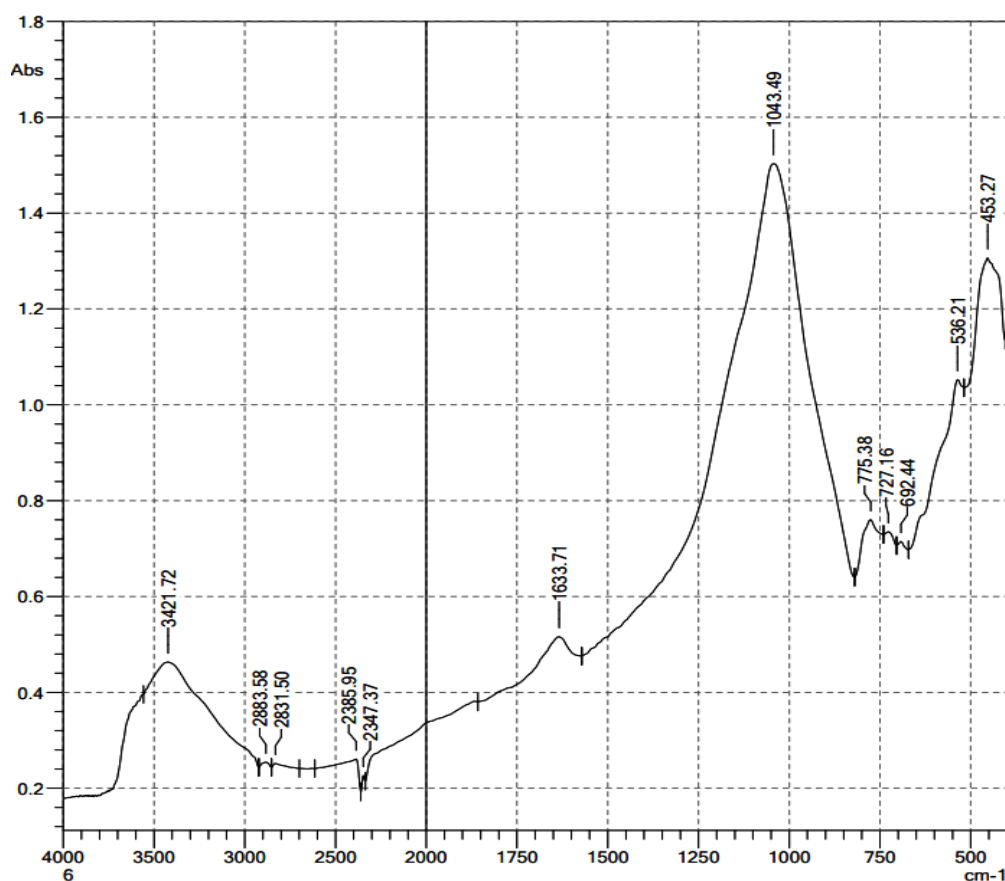


Figure.6 FTIR analysis of *Annona reticulata* – Chitosan adsorbent

3.4. Intra particle diffusion model

High regression coefficient (94%–96%) from experimental model constructed and reported in Table 6, it is believed that this kinetic model provides the most accurate description of the adsorption of *Annona reticulata*–chitosan isomers. Azo dye demonstrated a higher removal rate and adsorption loading compared to other isomers [77]. In some situations, the presence of methyl groups may speed up clearance. The intraparticle diffusion study shown in Table 6 are not adequate for interpreting experimental results because they have low R^2 values.

Table.6 Study of intraparticle diffusion

Column size (cm)	q_e / C	K1/ K2/Kdif.	R^2
6	2.513	-0.0063	0.9401
8	5.752	-0.0426	0.9532
10	6.935	-0.0137	0.9657

3.5. Regeneration study of adsorbent

Adsorption capabilities are impacted by the frequency of adsorbent recycling. After three cycles, their respective adsorption capacities are shown to be 21.56 mg/L, which is an 82.36%, 84.17%, and 88.62% reduction from their initial adsorption capacities [78]. The discoveries established that the adsorbent has strong cyclic adsorption presentation with a straightforward departure characteristic following adsorption as a result of its superior magnetic characteristics, which may more competently happen the action necessities.

3. Conclusion

Azo dye from textile effluent was analysed together with its adsorption onto biochar produced from *Annona reticulata*, as well as the volatilization of chitosan molecules for efficient adsorption in packed bed columns and dye adsorption breakthrough data. The effects of bed height, flow velocity, and initial dye attentiveness with packed bed adsorption were examined along with the possibility of column regeneration and reuse. The parameters such as cradle volume, amount transmission region, bed consumption, and adsorbent convention were assessed using the break through curves. For all operating circumstances, the length of the unoccupied bed was shorter than the adsorption column, which grows as the mass transfer zone expands. Three different sized columns were utilized to explore *Annona reticulata*'s ideal bed height. Hence, the adsorption capacity for a 6 cm column was 67.18%, an 8 cm column was 75.88%, and a 10 cm column was 94.37%. The adsorption models like the Bed Depth Service Thomas model and the Adam-Boharts models have been used to analyze the columns distinctive design characteristics. Using the origin software, the model's parameters have been determined. With R^2 0.975, Thomas and Adam-Boharts models were determined to be the best adsorption models out of four to examine column performance. Adam-boharts and Thomas models' average errors were calculated to be 0.0154 and 0.0263, respectively. According to the findings, the adsorption capacity in a 10 cm column is higher under optimal conditions, with a range of 94.37%. The column efficiency as measured by bed capacity up to the breaking point, the mass transfer zone, and bed utilization also demonstrates a significant improvement in the adsorptions process. SEM, XRD, and FTIR were used to analyze the surface properties of biochar made from *Annona reticulata* and volatilized by chitosan. In the mean of azo dye removal, the intra particle diffusion indicated the linear connection with adsorbent. The regeneration capacity was established, and it demonstrated that the adsorbent functions effectively over three study cycles.

Conflict of Interest

The authors declare no conflict of interest.

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