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Sustainable Textile Wastewater Treatment Using Biodegradable Chitosan for High-Efficiency Dye Removal

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Abstract

This study addressed a critical environmental issue by addressing the treatment of textile wastewater using chitosan, an eco-friendly bio-adsorbent. This approach aligns with global efforts to reduce pollution and promote sustainability in industrial processes. The non-biodegradable Congo Red (CR) dye, widely used in textile production, poses carcinogenic risks due to its potential to generate benzidine through complex reactions. Thus, the effective treatment of industrial effluent containing CR dye is crucial. A series of batch experiments were conducted to investigate the effects of adsorbent dose, contact time, initial dye concentration, and pH on the adsorption process. The study employed a variety of scientific techniques to characterize chitosan and evaluate its efficacy, including Scanning Electron Microscopy (SEM), Fourier-Transform Infrared Spectroscopy (FTIR), zeta potential analysis, X-Ray Diffraction (XRD), and Brunauer-Emmett-Teller (BET) surface area analysis. These techniques provided a comprehensive understanding of the adsorption mechanisms. The experiments revealed a maximum removal efficiency of 97.6% at an initial dye concentration of 40 mg/l, a chitosan dose of 2 g/l, an optimized contact time of 120 minutes, and a pH of 7. The characterization of chitosan confirmed its suitability for adsorption. The study was scaled up to practical application in a pilot plant for textile wastewater treatment, demonstrating substantial removal efficiencies for color, COD, BOD_5, and TDS, with average removal rates of 87.5%, 86.68%, 70%, and 81.2%, respectively. Furthermore, the research explored both the theoretical and practical aspects of using chitosan, demonstrating its viability as a wastewater treatment solution. By investigating an eco-friendly approach to wastewater treatment, this study made a significant contribution to the field.

Keywords: chitosan, textile wastewater, Adsorption, chemical oxygen demand.

1. Introduction

Recently, Contaminants from many different sources are getting into the environment, especially water, which has become a critical issue [1]. Increasing industrialization and urbanization have contributed to a worsening water crisis. Numerous industries, including the pharmaceutical, dye, fertilizer, smelting, mining, and textile dying industries, generate enormous quantities of wastewater [2]. One of the most complex and precarious pollutants is dye [3]. Worldwide, the consumption of dyes surpasses approximately 107 kg/year, with the textile industry being the largest consumer, accounting for the majority of this usage [4]. Synthetic dyes are widely used in printing and dyeing processes. These dye wastes pose serious dangers to ecosystem. Many of these wastes are poisonous and even cancer-causing [5]. Therefore, several countries have implemented numerous environmental regulations to eliminate any color that may be present in wastewater prior to its release onto surfaces or into public drainage systems [6]. For textile effluent treatment, numerous physical, biological, and chemical processes are applied [7]. An extensive range of techniques, including coagulation, filtration, precipitation, ozonation, and adsorption, have been devised and tested with the purpose of removing dyes [8-12]. Therefore, the aim of this study was to examine the use of an adsorption approach to remove dye from wastewater. Adsorption is a process that includes coming into contact between a rigid particulate phase and a free aqueous phase [13]. The rigid particulate phase has the ability to store or remove one or more solutes from the solution in a selective manner [14-19]. Biopolymers are natural polymers synthesized by living organisms, comprising monomer units linked together to form large, high molecular-weight molecules [20-23]. The three primary types include polynucleotides, polypeptides, and polysaccharides, with polysaccharides having a relatively simple structure [24-27]. Known as linear or branched polymeric carbohydrate molecules, they encompass cellulose, chitin, chitosan, starch, and alginate [28-29]. These biopolymers are particularly suitable for dye removal owing to their abundance, renewability, biodegradability, non-toxicity, surface tunability, and cost-effectiveness [30-33].Chitosan, a bio-adsorbent polymer, is commercially generated from chitin by de-acetylating, which is found in crustacean shells, insect exoskeletons, or fungal cell walls [31]. Chitosan possesses a notable abundance of amino (-NH_2) and hydroxyl (-OH) groups, resulting in a heightened adsorption capacity towards various contaminants [32]. The study was focused on Congo red dye for several reasons. Congo red is recognized as one of the most toxic dyes, posing severe environmental and health risks due to its complex molecular structure and resistance to

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biodegradation. Its popularity in the textile industry stems from its bright color, making it a preferred choice for dyeing fabrics. Consequently, it is frequently found in textile effluents, contributing to pollution in water bodies. In this case study, the textile factory where the wastewater samples were collected extensively uses Congo red dye in its production processes. By examining the adsorption mechanism of chitosan for Congo red, the study aimed to address a significant environmental challenge specific to this dying process while providing insights that can be applied to other similar industrial settings where Congo red is prevalent. This targeted approach ensures that the research is both relevant and impactful in developing effective wastewater treatment solutions. In this study, the viability of using chitosan as a bio-absorbent for reducing pollutants commonly found in textile wastewater, as color, COD, BOD_5 and TDS were assessed.

2. Methodology

2.1 Materials

Chitosan (white powder, high molecular weight, viscosity 3275 cp, deacetylation 82%, and density 0.2 g/ml, particle size 95% pass16 mm). Anionic azo dye (Congo red) (λ_{max} 497 nm and MW 696.66 g/mol).

2.2 Synthetic dye solution

Synthetic wastewater samples were prepared with dye concentrations ranging from 10 mg/l to 70 mg/l. This range was selected to encompass and slightly exceed the observed concentrations, ensuring a comprehensive analysis of the adsorption capacity and efficiency of chitosan under varied dye loads representative of real industrial effluents. This approach facilitates a robust evaluation of the treatment method's applicability and effectiveness across different contamination levels typical of textile industry wastewater.

2.3 Textile wastewater

Wastewater samples were obtained from textile effluent discharged by textile manufacturers in the industrial zone area. Five different samples were collected throughout the week at various intervals period from 9 am to 2 pm. For textile wastewater treatment, an integrated treatment approach comprising adsorption, sedimentation, and filtration stages was devised and executed, as indicated in Fig.1. The goal was to simulate these built treatment conditions and study their effect on water characteristics, including total dissolved solids (TDS), color, chemical oxygen demand (COD), and biological oxygen demand (BOD_5).

2.4 Chitosan characterization

Chitosan characterization was carried out using different analytical techniques. The surface area and pore volume of chitosan were measured using a Quantachrome NOVA touch analyzer. To examine the morphological properties of chitosan before and after dye adsorption, a scanning electron microscope (Tescan Essence Company-SEM) was employed. The zero-point charge for chitosan was determined using laser Doppler micro-electrophoresis and dynamic light scattering, with a Malvern Instruments Zetasizer. Fourier Transform Infrared was employed to characterize the functional groups of chitosan (Vertex 80V vacuum FTIR spectrometer). Wide-angle X-ray diffraction (XRD) analysis was conducted to assess the crystallinity of chitosan. Their diffraction patterns were recorded using a PANalytical X'Pert PRO XRD system. Chemical oxygen demand for all samples was measured by (COD) photometer. In this experimental work, biochemical oxygen demand measurements were conducted using the electrometric method with a dissolved oxygen meter (HANNA DO-5509 model).

2.5 Adsorption Study

The laboratory adsorption experiments utilized a synthetic Congo red dye solution at concentrations of 10, 40, and 70 mg/l. Chitosan dosages ranged from 0.5 to 3.5 g/l. The mixtures of chitosan and dye solution were stirred at a constant speed of 150 rpm using a magnetic stirrer, maintained at room temperature. The experiments explored a wide pH range from 2 to 12 to assess its impact on the adsorption process, with contact times ranging from 5 to 240 minutes. After the adsorption process, the dye concentrations in the solutions were measured using a spectrophotometer to determine the adsorption efficiency. This comprehensive approach allowed for the evaluation of various parameters affecting the adsorption capacity of chitosan for Congo red dye removal.

The efficiency of removal was obtained using Eq. (1) [33]:

$$E\% = ((C_0-C_F)/C_0) *100 \quad (1)$$

And, the amounts of dye adsorbed by chitosan (mg/g) were obtained using Eq. (2) [33]

$$Qe = (V (C_0-C_F) / M) \quad (2)$$

V (l) refers to solution volume, M (gram) refers to chitosan mass, and C_0 and C_F (mg/l) are the concentrations of dye in solution before and after adsorption, respectively.

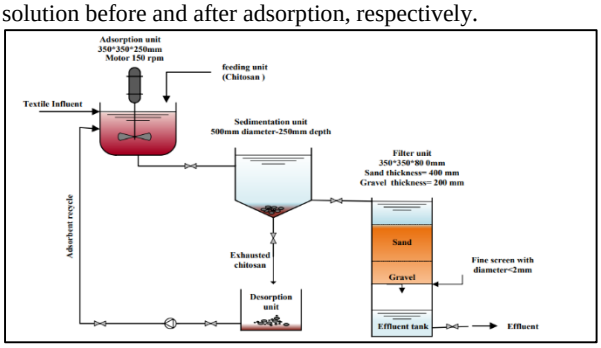

Fig.1. Textile effluent treatment unit.

2.6 Statical analysis

All experiments were conducted in triplicate. The data were analysed and reported as mean values ± standard deviations. This approach ensured high precision in measurements throughout the study, utilizing our calibrated instruments.

3. Results &discussion

3.1 Characterization of chitosan

3.1.1 Surface area (BET)

The surface area of chitosan particles was determined using BET surface area analysis. The results indicated that chitosan exhibited a surface area of 45 m^2/g, a pore volume of 0.11 cm^3/g, and an average pore size of 1.6 nm. These measurements suggest that chitosan particles possess a highly porous structure, significantly enhancing their surface area. This increased surface area is crucial for adsorption applications, as it provides more active sites for the interaction with adsorbates, thereby improving the efficiency of chitosan as an adsorbent.

3.1.2 SEM results

Chitosan's surface morphology was analyzed using Scanning Electron Microscopy (SEM). As shown in Fig. 2(a), the untreated (neat) chitosan surface exhibited a fibrous structure, indicating its natural, unaltered state. This fibrous appearance is characteristic of chitosan's polymeric nature, which provides a large surface area for adsorption. However, after the adsorption of Congo red dye, the surface of the chitosan appeared smooth, less porous, and more compact as shown in Fig. 2b. This change suggested that the dye molecules have successfully adhered to the chitosan fibers, filling in the pores and covering the surface irregularities. The smooth and compacted morphology indicated effective adsorption, where the dye molecules occupied the available adsorption sites on the chitosan, leading to a denser surface structure. This observation confirmed the ability of chitosan to adsorb and retain dye molecules, thereby demonstrating its potential as an effective adsorbent for wastewater treatment.

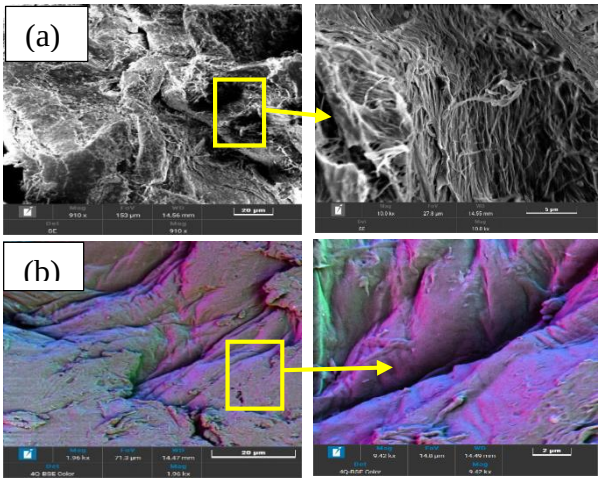

Fig.2. The surface image of (a) Neat chitosan and (b) Chitosan/CR after adsorption.

3.1.3 ero-point charge

Understanding the zeta potential is crucial for optimizing process efficiency. The pH_{zpc} of chitosan was determined to be 6.5. At pH levels below the pH_{zpc}, the surface carries a positive charge due to the protonation of numerous amine groups within the chitosan polymeric matrix. Conversely, at pH levels above the pH_{zpc}, the surface becomes negatively charged as amine groups undergo deprotonation in an alkaline environment.

3.1.4 FTIR results

Neat chitosan's FTIR spectra shows distinct peaks that are associated with different functional groups. As shown in Fig. 3(a), broad bands in the 3200–3500 cm^{-1} spectrum correspond to the stretching vibrations of hydroxyl (OH) and amino (NH_2) groups, which enable chitosan to form hydrogen bonds with polar molecules. The band at 2900 cm^{-1} indicates C-H stretching vibrations. The absorption band at 1150 cm^{-1} arises from the asymmetric stretching of the C-O-C bridge, while the band at 1024 cm^{-1} represents C-O stretching. The band around 850 cm^{-1} highlights the presence of NH_2 groups. These distinct functional groups in the chitosan structure make it an excellent adsorbent for various substances. Following the adsorption process, as depicted in Fig. 3(b), changes in wavenumber or intensity at peaks corresponding to the functional groups involved in dye adsorption may occur. The absorbance intensity at 1579 cm^{-1} increases potentially indicating the presence of amino groups from adsorbed Congo Red. There is a decrease in absorbance intensity at 1654 cm^{-1}, associated with C-C stretching. The high absorbance intensity at 1380 cm^{-1} suggests the presence of N-H, likely formed through hydrogen-bonding interactions between chitosan hydroxyl groups and the azo group of the dye molecules. Additionally, a peak at 1220 cm^{-1} is detected, possibly attributed to the C-N bond from the amines of Congo Red. Finally, shifts in the peaks at 890 ,1024, and 1150 cm^{-1} are observed, which may be linked to the SO_3 groups of Congo Red. This information confirms the dye adsorption process on the chitosan surface.

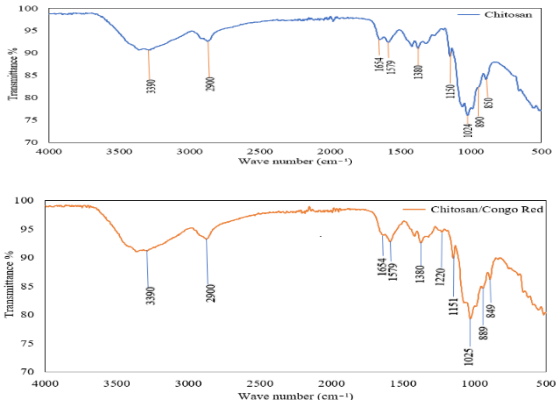

Fig.3. FTIR spectrum for (a)Neat chitosan and (b) chitosan/Congo Red.

X-Ray diffraction (XRD) analysis

The X-ray diffraction (XRD) pattern of pure chitosan, shown in Fig. 4, reveals several key peaks at 2θ values of 10°, 20°, 23°, 25°, and 29°. These peaks are indicative of chitosan's crystalline structure. Specifically, the peak at 10° corresponds to the hydrated crystalline form of chitosan, reflecting the presence of water molecules within the crystal lattice. This hydrated form impacts the material's flexibility and solubility. The peak at 20° is attributed to the anhydrous crystalline form, representing the ordered arrangement of chitosan polymer chains without water. This anhydrous form contributes to the rigidity and strength of the material. The additional peaks at 23°, 25°, and 29° further confirm the crystalline nature of chitosan, indicating various levels of crystallinity and different crystal orientations. The crystalline structure of chitosan plays a crucial role in its physical properties, such as mechanical strength, thermal stability, and adsorption capacity. The ordered arrangement of polymer chains, as evidenced by these distinct peaks, ensures that chitosan maintains a robust framework that can effectively interact with and adsorb dye molecules, making it a suitable candidate for applications in wastewater treatment and other fields.

3.2 Effect of pH on removal %

The maximum removal effectiveness of Congo red (96%±0.6) was observed at pH 6 as shown in Fig.5. However, it was noted that the removal effectiveness decreased at lower pH values, particularly at pH 4. This decrease can be attributed to the dissolution of neat chitosan in strongly acidic solutions. Zeta potential analysis was conducted to elucidate the influence of pH on the chitosan surface charge. It was found that chitosan exhibited a positive charge in acidic media, while Congo red dye contains ($-SO_3^-$ Na^+) groups, which impart a negative

charge. The increase in removal efficiency under acidic conditions can be attributed to the electrostatic interaction between the protonated amino groups in the chitosan structure and the negatively charged dye molecules.

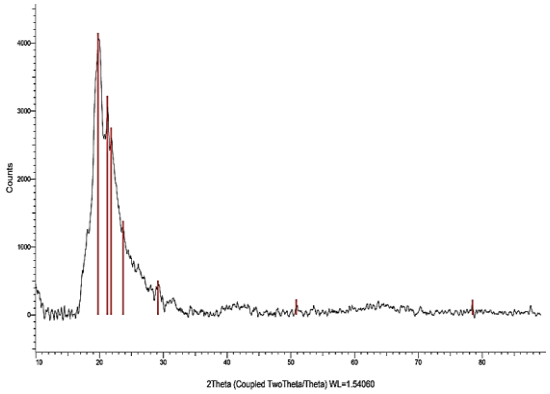

Fig.4. The XRD spectrum of Chitosan.

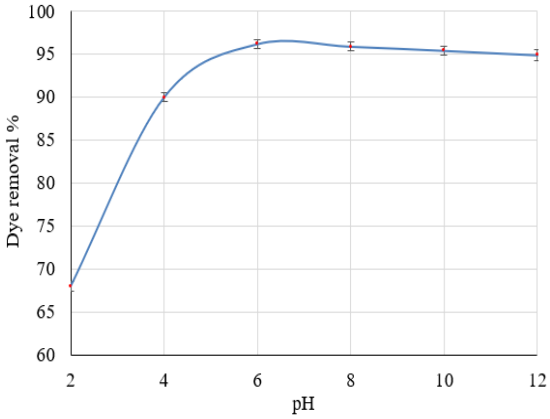

Fig.5. Effect of pH solution on Removal% (Dye concentration: 40 mg/l, dose1g, contact time: 240 min, and temperature: 29 ºC).

3.3 Effect of chitosan dose on removal%

As depicted in Fig. 6 (a) and (b), the removal efficiency of Congo red dye improved with increasing chitosan dosage until reaching equilibrium, attributed to the expanded surface area available for adsorption. The impact of dosage on removal efficiency was studied across various initial dye concentrations, with a consistent duration of 120 minutes and pH maintained at 7. It was found that with the addition of 1 g of chitosan, the removal percentage reached 99%±0.4 and equilibrium loading 9.9±0.04 mg/g for a solution with an initial concentration of 10 mg/l. Similarly, a high removal percentage of 97.6% ±0.6 was achieved with 2 g of chitosan and equilibrium loading 19.52±0.12 mg/g for an initial concentration of 40 mg/l. At a dose of 3.5 g/l, the maximum removal percentage reached 96±0.3% and equilibrium loading 19.2±0.06 mg/g for an initial concentration of 70 mg/l.

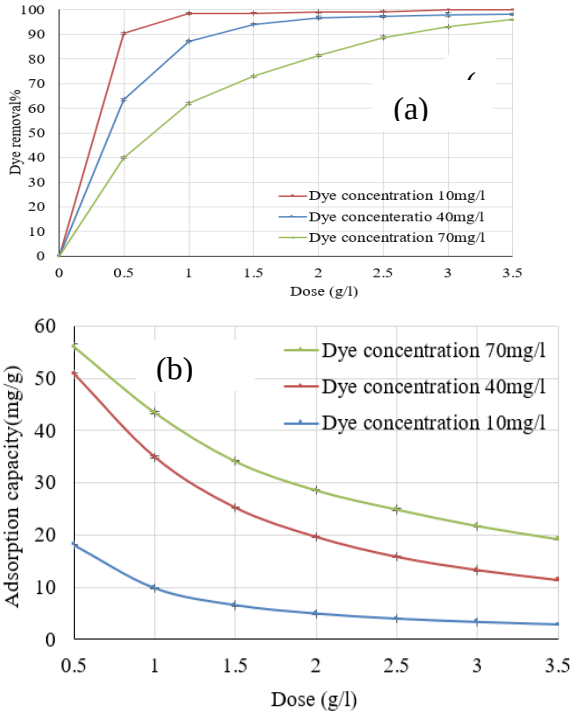

Fig.6. The effect of chitosan dose on removal%(a)and adsorption capacity(b). (contact time:120min, pH=7, temperature: 29°C and 150rpm)

3.4 Effect of time on removal%

The removal efficiency notably increases over time, as depicted in Fig. 7, due to prolonged contact durations that allow Congo red dye molecules to access the inner active sites of chitosan effectively. Experimental results indicated that as the contact time increased, dye removal efficiency also increased, reaching optimal levels. Specifically, at a contact time of 120 minutes and a chitosan dose of 2 g/l, the equilibrium concentration dropped to 0.05 mg/l with a removal efficiency of 99.5%±0.3 and an optimal loading capacity of 4.975±0.015 mg/g for an initial dye concentration of 10 mg/l. Similarly, for an initial dye concentration of 40 mg/l, the equilibrium concentration decreased to 0.952 mg/l with a removal efficiency of 97.6%±0.6 and an optimal loading capacity of 19.52±0.12 mg/g. At a higher initial dye concentration of 70 mg/l, the equilibrium concentration decreased to 13.65 mg/l with a removal efficiency of 80.5%±0.45 and an optimal loading capacity of 28.175±0.16 mg/g.

3.5. Effect of initial dye concentration on removal (%)

In Fig. 8(a) and (b), the dye removal percentage decreases with increasing initial dye concentration, while the adsorbent loading increases under constant adsorbent dose and contact time. For an adsorbent dose of 0.5 g/l, the removal efficiencies were (90 ± 0.5, 65 ± 0.4, and 38 ± 0.4) for initial dye concentrations of 10, 40, and 70 mg/l, respectively. At an adsorbent dose of 2 g/l, the removal efficiencies were (99.5 ± 3, 97.6 ± 0.6, and 80.5 ± 0.45), and at 3.5 g/l, they were (99.9 ± 0.1, 98.1 ± 0.5, and 96 ± 0.3), respectively. These findings underscore the close relationship between removal percentage and solution concentration.

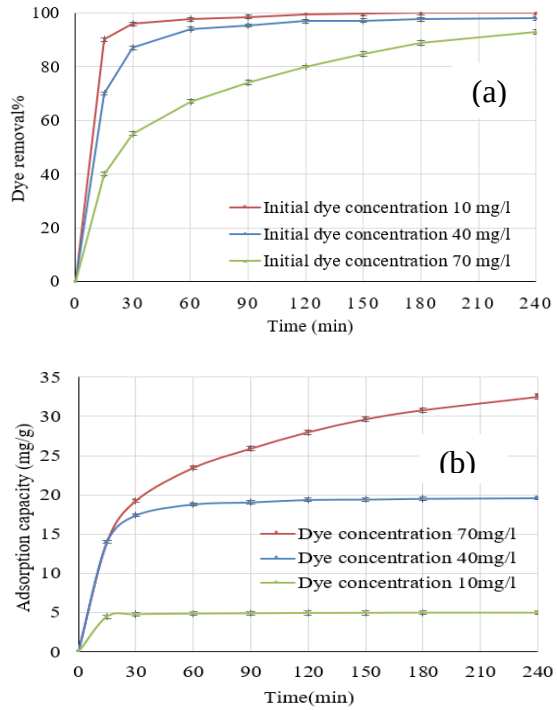

Fig.7. The effect of contact time on removal %(a) and adsorption capacity(b).
(dose: 2g, pH=7, temperature: 29°C and 150 rpm)

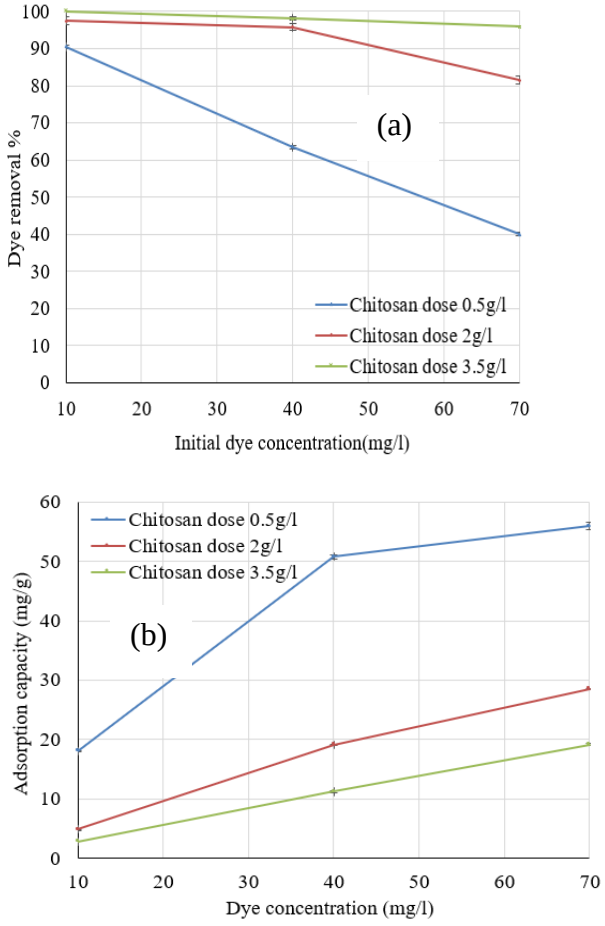

Fig.8. The effect of dye concentration on removal%(a) and adsorption capacity(b).
(Contact time:120 min, pH=7, temperature: 29°C and 150 rpm)

3. Adsorption isotherm

Understanding how Chitosan interacts with CR dye molecules requires studying the adsorption isotherm. In this study, non-linear equilibrium isotherm models such as Freundlich and Langmuir were used to evaluate Chitosan's adsorption capacity for CR dye. The equilibrium models are described by Freundlich's and Langmuir's nonlinear equations, are given by Eqs. (3) and (4), respectively [25-27, 34].

$$Qe=K_f(Ce)^{1/n} \quad (3)$$

$$Qe= (Ce\ Q_m\ K_L) / (1+C_e\ K_L \quad (4)$$

The parameter Q_e (mg/g) represents the amount of Congo Red dye adsorbed per unit mass of chitosan at equilibrium, while Ce (mg/l) indicates the equilibrium concentration of CR dye. The constant 'n' characterizes the Freundlich isotherm model, reflecting adsorption intensity. Q_m (mg/g) denotes the maximum adsorption capacity of CR dye by chitosan, and K_L (l/mg) is the Langmuir constant, indicating the strength of interaction between the adsorbate and the adsorbent surface. These parameters are crucial for assessing the efficiency of chitosan in removing CR dye from aqueous solutions.

The Freundlich isotherm model describes the adsorption process involving multilayer mechanisms, suggesting that Congo Red dye molecules can adsorb onto a heterogeneous surface, forming multiple layers. In contrast, the Langmuir model assumes monolayer adsorption on a homogeneous surface with a finite number of active sites. The parameters of these isotherm models are detailed in Table 1.

The Freundlich model exhibited the highest correlation, demonstrating an R^2 value of 0.9821, which signifies heterogeneous surface adsorption of CR dye. This heterogeneity suggested that the active sites on the chitosan surface vary in their affinity for dye molecules, indicating multiple mechanisms such as electrostatic interactions, hydrogen bonding, and van der Waals forces. Thus, chitosan showed promise as an eco-friendly adsorbent for efficiently removing various anionic dyes and contaminants from industrial wastewater.

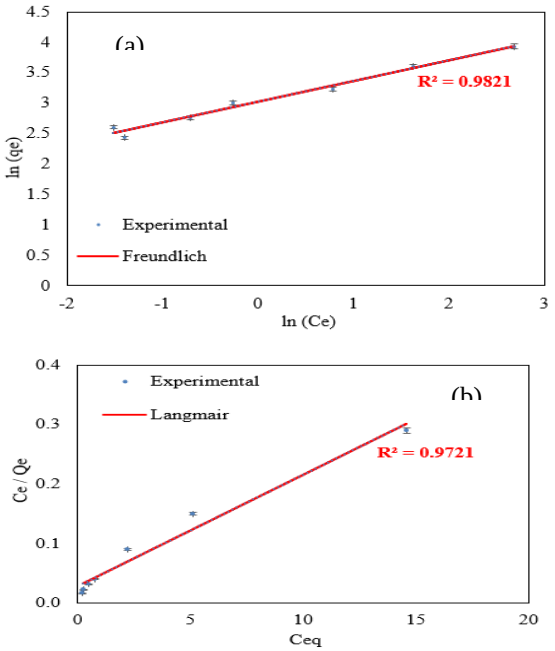

Fig.9. adsorption isotherm models of chitosan for CR removal(a)Freundlich and (b) Langmuir.

Table 1 The Langmuir and Freundlich parameters for CR adsorption.

Langmuir			Freundlich		
K_L (l/g)	Q_m (mg/g)	R^2	K_F (mg/ g)	n (g/l)	R^2
0.66	53.47	0.9721	20.45	2.94	0.9821

4. Adsorption kinetics

Understanding adsorption kinetics is crucial for comprehending the behaviour of adsorption. This study utilized the pseudo-first order (PFO) and pseudo-second order (PSO) models to analyse the kinetics of chitosan adsorption. The equations for these nonlinear models, represented as Eqs. (8), and (9) were employed respectively [25-27,35,36].

$$\text{Ln } (Q_e/Q_t) = \ln Qe - (K_1 t) \quad (5)$$

$$(t/Q_t) = (1/ (K_2 Q_e^2)) + (t/Q_e) \quad (6)$$

In this study, Q_e represents the amount of Congo Red dye adsorbed by chitosan at equilibrium, while Q_t refers to the amount adsorbed at time (t). The kinetic model parameters, denoted as K_1 (l/min) for PFO and K_2 (g/mg· min) for PSO, along with their respective correlation coefficients (R^2), are detailed in Table 2. Particularly noteworthy, the PSO model demonstrated a high R^2 value and accurately predicted Q_e values comparable to experimental data. This indicates that the adsorption of CR dye onto chitosan followed the PSO model, suggesting a chemisorption process. Chemisorption involves strong electrostatic interactions between the positively charged chitosan surface, characterized by protonated amino groups, and the sulfonic groups of CR dye molecules.

5. Textile wastewater

The treatment system was designed and constructed, consisting of an adsorption tank, sedimentation tank, and sand filter unit. These tanks are equipped with electrical motors to assist in mixing the textile wastewater and the adsorption material. The optimal operating conditions established by the batch-adsorption investigation are as follows: Chitosan doses in the range of 1- 2.5 g/l for wastewater with various dye concentrations up to 70 mg/l, an agitation time of 2 hours; an agitation rate of 150 rpm; and a pH of 7 for the adsorption process. The chitosan adsorbent was allowed to settle for 15 minutes. The wastewater was then transferred to the sand filter unit. An investigation will be conducted to examine how operational parameters affect the removal efficiencies of COD, BOD_5, color, and TDS. The process was used under optimal removal conditions. The properties of the textile wastewater are indicated in Table 3. Standards and specifications of industrial liquid effluent which is licensed to discharge into brackish or saline surface water bodies [37], listed in Table 3.

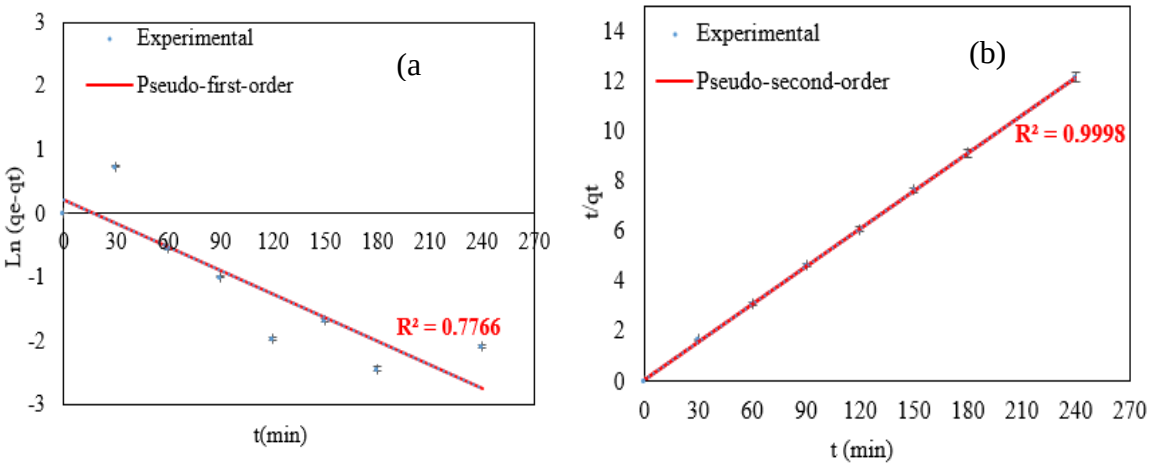

Fig.10. Adsorption kinetics models of chitosan for CR removal(a)Pseudo- first- order and(b)Pseudo second order.

Table 2 Kinetics models parameters for the CR adsorption on chitosan

Pseudo-first-order			Pseudo-second-order		
K_1 (l/min)	q_e (mg/g)	R^2	K_2 (g/ mg· min)	q_e (mg/g)	R^2
0.00005	1.23	0.7766	0.0309	19.84	0.9998

Table 3 The textile wastewater properties.

Textile wastewater (samples)	Contaminates					
	Dye concentration (mg/l)	Color (Pt /C_o)	COD (mg/l)	BOD_5 (mg/l)	TDS (mg /l)	Temperature (°C)
Sample 1	45.8	816	1323	121	1900	28.7
Sample 2	23.1	402	791	118	1345	29.3
Sample 3	57.9	1020	2200	187	2300	28.1
Sample 4	7.7	102	555	67	1348	28
Sample 5	33.3	509	1210	180	1735	28.4
Low No.48 for year 1982	----	----	< 100	< 60	< 2000	35 °C

6.1 Effects of treatment parameters on organic matters removal

The influent COD levels ranged from 555 to 2200 mg/l, with an average of 1215.8 mg/l, as determined from the analysis. After treatment, the effluent COD levels ranged from 49 to 395 mg/l, averaging at 190.2 mg/l. This signifies a significant reduction in COD levels, with an average removal efficiency of 86.68%, as depicted in Fig. 11. The analysis underscores the effectiveness of the treatment process in substantially lowering COD concentrations, highlighting its impact on improving wastewater quality.

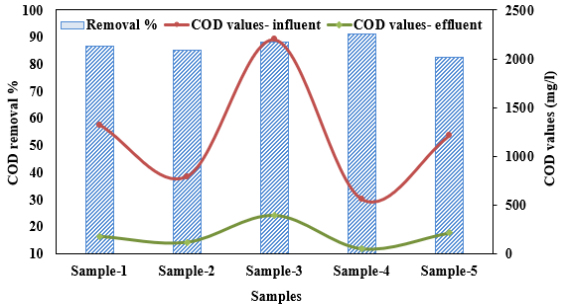

Fig.11. The treatment effect on COD.

6.2 Effects of treatment parameters on BOD_5

The influent BOD_5 levels ranged from 180 to 67 mg/l, averaging 135 mg/l, based on the analysis conducted. After treatment, the effluent BOD_5 levels varied from 22 to 57 mg/l, with an average of 40 mg/l. This reflects a substantial reduction in BOD_5 levels, indicating an average removal efficiency of 70%, as shown in Fig. 12. The results underscore the effective performance of the treatment process in significantly decreasing BOD_5 concentrations, thus improving the quality of the treated wastewater.

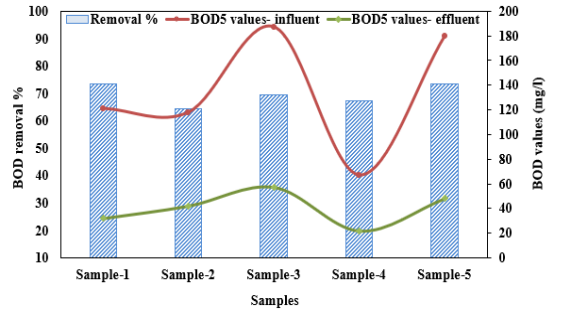

Fig.12. The treatment effect on BOD_5.

6.3 Effects of treatment parameters on dye removal

The dye concentration levels in the influent samples fluctuated between 7.7 and 57.9 mg/l, with an average of 33.56 mg/l, as determined by the analysis. Following treatment, the effluent samples exhibited dye concentration levels ranging from 0.62 to 5.15 mg/l, averaging of 3.9 mg/l. The average dye removal was 89.13%, indicating a substantial improvement in water quality as illustrated in Fig.13.

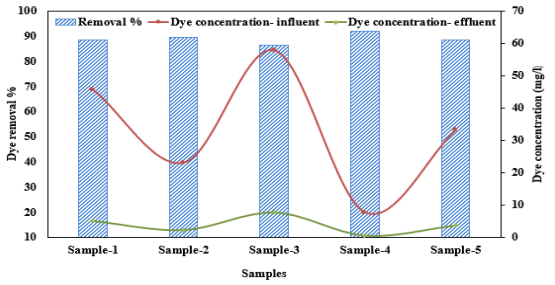

Fig.13. The treatment effect on Dye concentration

6.4 Effects of treatment parameters on TDS removal

The influent TDS levels ranged between 1345 and 2300 mg/l, averaging 1725 mg/l based on the analysis. After treatment, the effluent TDS levels varied from 232 to 450 mg/l, with an average concentration of 326 mg/l. This signifies a significant reduction in TDS levels, demonstrating an average removal efficiency of 81.2%, as shown in Fig. 14. These findings highlight the effective capability of the treatment process in lowering TDS concentrations, contributing to improved water quality outcomes.

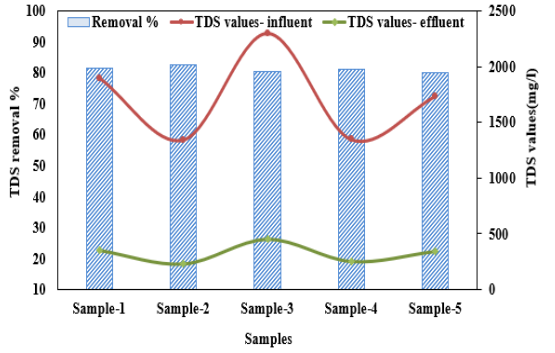

Fig.14. The treatment effect on TDS

6.5 Effects of treatment parameters on color removal

The initial color levels in the influent samples ranged from 1020 to 102 Pt/Co, with an average of 586 Pt/Co, based on the analysis. After treatment, the effluent color levels ranged from 154 to 9 Pt/Co, averaging78.8 Pt/Co. This indicates a substantial reduction in color concentration, with an average removal efficiency of 87.5%, as depicted in Figure 15. These results underscore the effectiveness of the treatment process in significantly decreasing color levels, thereby improving the overall quality of the treated wastewater.

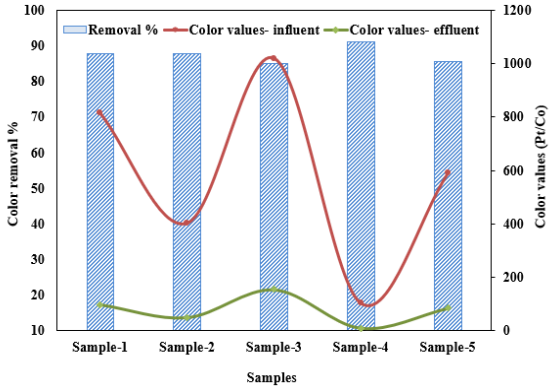

Fig.15. The treatment effect on color.

Regeneration and reusability of chitosan

Reusing and recovering the adsorbent is essential for significantly reducing the cost of the treatment process. In this study, chitosan loaded with Congo Red (CR) was prepared, washed to remove the adsorbed dye, and then dried. Desorption was carried out using 0.5 M NaOH, followed by thorough washing and drying of the chitosan. The regenerated chitosan was reused for subsequent CR adsorption cycles. Notably, after three cycles, the CR removal efficiency remained above 50%, highlighting the sustainability and cost-effectiveness of this wastewater treatment method.

7. Adsorption mechanism between chitosan and CR

The adsorption mechanism between chitosan and Congo red dye primarily involves electrostatic interactions, where the positively charged amino groups of chitosan attract the negatively charged sulfonate groups of Congo red. Additionally, hydrogen bonding occurs between the hydroxyl and amino groups of chitosan and the nitrogen color as shown in Table 4, chemical oxygen demand (COD), biological oxygen demand (BOD5), and total dissolved solids (TDS), under different operational conditions underscores its versatility and effectiveness. and oxygen atoms of Congo red. Van der Waals forces and π-π interactions between the aromatic rings of Congo red and chitosan further contribute to the adsorption process. The adsorption involves the initial external diffusion of dye molecules to the chitosan surface, followed by internal diffusion into the pores of the chitosan. The efficiency of this process is highly dependent on the pH of the solution, as lower pH values enhance protonation of chitosan, increasing electrostatic attraction with the anionic dye.

8. Comparison between chitosan biopolymer and adsorbents

The utilization of chitosan for dye adsorption in textile wastewater treatment offers a highly advantageous approach compared to other adsorbents. chitosan is sustainable, with the potential for regeneration and reuse, which further reduces treatment costs. Its efficiency in removing various pollutants, including

This makes chitosan a superior choice for addressing the complex issue of dye pollution in textile wastewater, promoting cleaner production and compliance with stringent environmental regulations.

Table 4 Comparative study between chitosan and other adsorbent.

materials	Adsorption condition	Contaminates	Removal	References
pine bark	pH=7, Temperature=25ºC Dye concentration=5mg/l, Time 160min, Dose=10g/l	Azo dye	80%	[38]
modified banana leaves	PH=2, Temperature=28ºC, Dye concentration=,50mg/l Time=120min, Dose=2g/l	Anionic dye	79%	[39]
modified walnut shell	PH=2, Temperature=28ºC, Dye concentration=50mg/l, Time=120min, Dose=2g/l	Anionic dye	97%	[40]
Chitosan powder	PH=5, Temperature=28ºC, Dye concentration=500mg/l, Time=300min, Dose=3.3g/l	Anionic azo dye	95.56%	[41]
Chitosan	PH=7, Temperature=29ºC, Dye concentration=40mg/l, Time=120min, Dose=2g/l	Anionic dye	97.6%	Current study

9. Cost estimation

Throughout the research study, efforts were made to estimate the cost of chitosan adsorbents. The expenses associated with each process were meticulously calculated and presented in Table 5. Additionally, the overall cost for the preparation of the adsorbent. It was determined that the total cost to prepare 1 kg of chitosan adsorbent was approximately 2.09**$**. This comprehensive cost analysis is crucial for evaluating the economic feasibility of using chitosan as an adsorbent in wastewater treatment.

Table 5 The cost estimation for 1 Kg chitosan adsorbent.

Adsorbent type	Initial concentration (mg/l)	Adsorption capacity (mg/g)	Removal efficiency (%)	Optimum conditions		price ($/kg)	Adsorbent cost / 1g dye ($)	Cost of adsorbent /m^3 ($)
				Optim	Optim			
Chitosan	10	19.52	99%	0.5	120	2.09	0.107	1.07

It was found that the cost for removing 1 g of Congo red dye from synthetic wastewater using chitosan varies with the initial dye concentration. Specifically, the cost is 0.107 **$**. for an initial concentration of 10 mg/l, as shown in Table 6.

Table 6 Summary of adsorbents for Congo Red dye removal

process	Price ($)	Electrical consumption	Labor ($)	Maintenance ($/yr	Indirect cost	Working hours	Device lifespan	Productivity (Kg/	Unit cost ($/K
Transportation and handling	49036.45/ Trip	---	41.66	---	8826.6	---	---	27600/ Trip	2.09

As listed in Table 7, the cost for treating 1 m³ of industrial wastewater containing Congo red dye with chitosan varies depending on the initial dye concentration. For an initial concentration of 10 mg/l, the treatment cost is 0.18 **$**. This demonstrates the increasing cost associated with higher concentrations of dye in the wastewater. In comparison to other adsorbents, as listed in Table 8, the cost of commercial chitosan is relatively low, making it an economically viable option for wastewater treatment. Chitosan not only offers effective adsorption capabilities but also provides a cost advantage, which is crucial for large-scale industrial applications. The affordability of chitosan, combined with its high efficiency in dye removal, positions it as a preferred choice over more expensive adsorbent. Detailed cost analyses, such as those presented in this study, highlight the financial benefits of using chitosan, thereby supporting its widespread adoption in treating industrial effluents.

Table 7 Cost of treatment for Congo Red dye removal from the industrial wastewater for influent 50 m³/day.

Adsorbent	Initial concentration (mg/l)	Initial investment ($)	Cost of adsorbent (6 cycle)/m³ ($)	Cost of adsorbent /year ($)	Total cost of adsorbent /lifespan ($)	Total operation costs ($)	Total life cycle cost	Productivity (m³)	Total cost /m³ ($)
chitosan	10	1250	0.178	3248.5	81212.5	312.5	82775	456250	0.18

Table 8 Comparison of the cost of treating wastewater using chitosan and other adsorbents.

Adsorbent	Target pollutant	Initial concentration of pollutants	Adsorption capacity(mg/g)	Cost($/g)	Ref
Coconut shell biochar	Basic Red 09	25	10	0.7037	[42]
AC from Sugarcane Bagasse	Methylene blue	15	29.1	0.0021	[43]
Chitosan-calcite	Phosphorus	1	21.36	0.2646	[44]
Chitosan	Congo Red	10	19.52	0.0029	Current study

10. Conclusion

The use of chitosan as a bio-adsorbent for textile wastewater treatment has shown significant promise. This study evaluated the effectiveness of a treatment system incorporating adsorption, sedimentation, and filtration units for managing textile wastewater. Results indicated substantial reductions in COD, BOD_5, color, and TDS levels in real textile wastewater, decreasing from 2200 mg/l, 187 mg/l, 1020 pt/Co, and 2300 mg/l in influent wastewater to 395 mg/l, 57 mg/l, 154 pt/Co, and 450 mg/l, respectively. The average removal efficiencies were 86.68% for COD, 70% for BOD_5, 87.5% for color, and 81.2% for TDS. These findings highlight the potential of chitosan in industrial wastewater treatment. Additionally, the study demonstrated that the proposed system could enhance the removal efficiency of COD, BOD_5, color, and TDS from wastewater under various environmental conditions.

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