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The Removal of Methylene Blue Dye from Industrial Wastewater by Using Chitosan

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ABSTRACT

The paper focuses on treating industrial wastewater contaminated with methylene blue using chitosan powder as an adsorbent. Chitosan is well recognised in diverse fields and readily available at low cost. Chitosan is derived from marine fish scale waste. The study used methylene blue dye at various concentrations ranging from 50 to 200 mg / L. Experimental experiments were carried out at different temperatures ranging from 25 to 40 °C to evaluate the efficacy of chitosan in dye removal. Kinetic and kinetic equilibrium experiments were performed, and the thermodynamic properties of the system were studied. The results showed that chitosan effectively removed the methylene blue die from the polluted industrial wastewater. At 25 °C, the removal efficiency was found to be 94%. Overall, this study demonstrates the possibility of using chitosan as an adsorbent to treat industrial wastewater contaminated with methylene blue. It was found through the equipoise test that the adsorption process occurs through the first 30 minutes of the adsorption process start of the adsorption process. Chitosan was an excellent and effective substance in removing dye contaminants from industrial water. It was observed that Freundlich's law obeyed the absorption process, and the error rate was much better than the Langmuir model. Simultaneously, the kinetics followed the second-order model better than the first-order model with R2= 0.999.

KEYWORDS: Blue Dye, chitosan, wastewater, kinetic, Equilibrium.

1 INTRODUCTION

Water contamination from various dangerous substances, which may be poisonous to humans, has severely threatened the ecosystem. The group of dyes is among the difficult ones [Albright,2016]. They are widely utilised in various industries, including those that produce drugs, cosmetics, paper, print, leather, plastics, dyes, and textiles [Inyinbor, Adebesin,2018]. Shades come in three types which are acidic anionic, basic cationic, and nonionic dispersion dyes. Most of these colours are members of the aromatic azo group, which can cause human mutagens, cancer, allergic dermatitis, and skin irritation [Lellis,2019][Yaseen,2019]. They frequently withstand light, heat, and oxidants because of their synthetic origin and intricate aromatic molecular structure [Forgacs,2004][Seow,2016]. They stand out for having vibrant colours that obscure light and make it difficult for aquatic life to engage in photosynthesis [Kyzas,2004]. Finding effective techniques for removing the paint from wastewater before it interacts with naturally occurring, unpolluted water bodies is essential because colour contamination can have severe consequences. There are ways to decontaminate water from conventional treatment methods, such as electrocoagulation. As indicated by [Hawass Aljabri,2024] in their study explaining the effect of mono on electrocoagulation in the removal of heavy metals from wastewater, flocculation, sedimentation, ozone, catalytic oxidation, electrochemical destruction, membrane filtration, ion exchange, reverse osmosis, irradiation, biological treatment, and adsorption [Yaseen,2019]. The adsorption method was used to treat metal-contaminated water and remove lead using carbon-activated rice husks from wastewater, which was reinforced by [Khashan, Mohammad, 2020] with a study. Ultrasound-assisted adsorption was used to treat methylene blue [Oatta, Mohammed, 2021], indicating this method is a new approach in wastewater treatment. However, only a few of these methods can meet discharge limits independently, while others generate significant amounts of secondary waste [Azha, 2014]. For its friendly use, effective cost, adaptability, and tolerance to hazardous contaminants, adsorption is considered a successful treatment strategy. Though commercial activated carbon is the preferred adsorbent for colour removal, its widespread use is limited due to its high cost [Azha, 2017]. Therefore, it is necessary to seek out alternative ingredients that are both effective and affordable. Several contemporary adsorbents include fish scales (chitosan), fly ash, clays (kaolinite, montmorillonite, bentonite, zeolite, etc.), wheatgrass, sawdust, peat, nut shells, sludge, and activated sludge, as they produce minimal residual waste [Martins,2013].

2 EXPERIMENTAL WORK

2.1 Materials

All chemicals applied in the empirical work are highly transparent and were available in the laboratories of the Chemistry department of the College of Engineering except the fish scales, which were collected from Samawah city of Al-Muthanna governorate. It was used to conduct adsorption operations on it.

2.2 instrument used for the process

The schematic diagram and image of the apparatus utilized for the adsorption process are shown in Figure (1)

- The adsorption instrument consists of a 500 ml boiling flask that is used as an absorption chamber.
- To measure the adsorption temperature, a glass and digital thermometer were placed within the flask.
- A Pyrex glass recycling condenser. Is installed in the flask to ensure that no fumes from the adsorption mixture are delayed. The reflux condenser's working fluid was regular tap water.
- The water bath for the adsorption blend was a 1000 mL Pyrex glass beaker.
- To achieve proper insulation, a coating of glass wool is used. A magnetic hot plate is used to supply the device with the appropriate heat and to guarantee that the adsorption mixture is thoroughly mixed throughout this isothermal testing setup.
- A thermocouple connected to a digital recorder within the Beaker continuously measures the water bath's temperature.

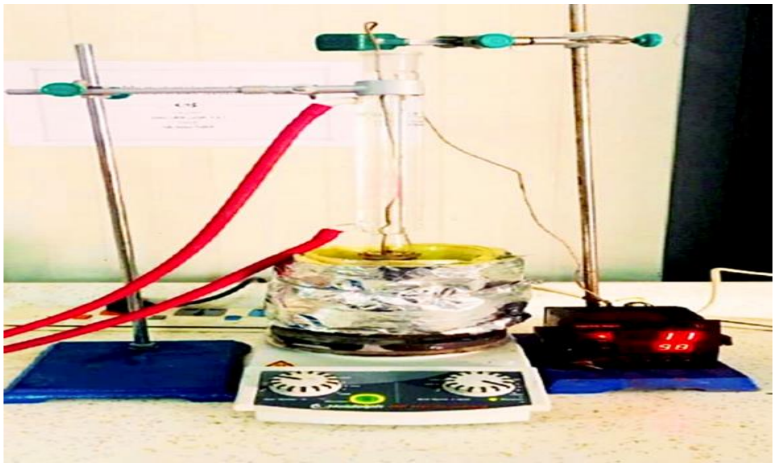

Figure 1. Schematic diagram of the adsorption process apparatus

3 ADSORPTION

Each type of dye (methylene blue) was weighed out to make stock solutions of 0.05 g each; after that, it was dissolved in 100 ml of distilled water. As a result, solutions with the required concentrations were produced by continuously diluting them with distilled water following the dilution rule [Lacher, 2010] Fig (2).

$$C1 * V1 = C2 * V2$$

Equation 1

Where:

C1: The initial concentration of the solution (in mg/L).

C2: The solution's final concentration (in mg/L) following dilution.

V1 is the initial volume of the solution (in litres).

V2: The liquid volume of the diluted solution.

Figure 2. Image of the typical dye solutions for methylene blue that have been created.

Table 1. Properties of methylene blue.

Properties	Dye methylene blue
Molar mass	319.85 g/mole
Chemical structure	C16H18ClN3S
Solubility at 20 °C	Water and ethanol
Brand	Sigma-Aldrich

3.1 Equilibrium of Adsorption

The use of characteristic isothermal modelling together with isothermal information analysis represents a significant improvement in the process of selecting the best applicable model for the design objectives. For a given adsorbent, an equipoise data relationship that uses a notional or empirical mode to explain and foresee the grade of adsorption is used to determine the maximum adsorption limit [Foo, 2010]. Figure (3) shows the equilibrium adsorption isotherms curves of methylene blue essential tincture adsorbed on the roof of a prefabricated chitosan adsorbent. At different temperatures (25, 30, 35, and 40 °C), these curves were generated for the concentricity range (50–200 ppm).

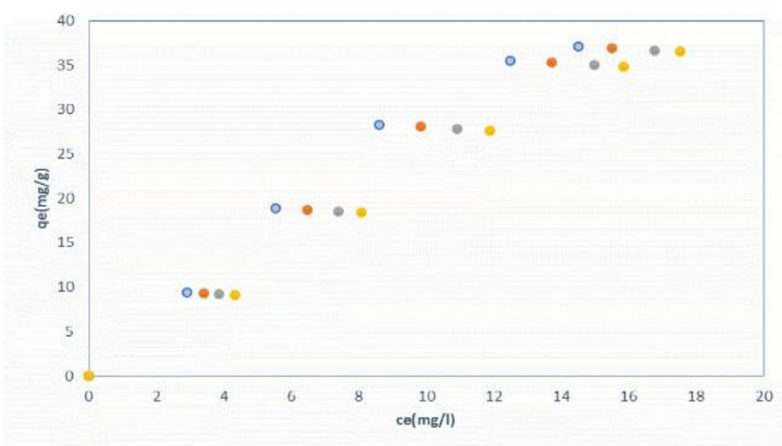

Figure 3. Adsorption equipoise (isotherms) for methylene_blue adsorbed on the chitosan at various heats.

These results demonstrate the proportionality between dye concentrations in the solution phase and absorption. This is evident from the way conventional absorption-type isotherms are formed. Therefore, the dye concentration on the surface of the absorbent material will rise with mounting dye concentricity in the solution. However, at higher dye concentrations in solution, these ratios are less pronounced because the absorbent has reached its maximum capacity. The numbers in Table (2) represent the top properties of chitosan generated.

Table 2. Extreme capacities of chitosan for methylene blue.

Temp. ◦C	Methylene blue	
	Ce (mg/L)	Qe (mg/g)
25	14.512	37.0976
30	15.514	36.8972
35	16.756	36.6488
40	17.521	36.4958

The correlation of experimental data on methylene blue adsorption on chitosan was performed using the Langmuir and Freundlich isothermal (adsorption models). These models were employed in the current experiment as they [Dada, 2012] are among the most well-known equations that represent the adsorption of a solute in an aqueous solution onto a solid adsorbent. Langmuir isotherms are mathematical representations of a single layer of solute particles adsorbed on a solid adsorbent. According to the Langmuir adsorption theory, which explains the surface of solid adsorbents, this is based on the homogenous surface assumption. The Langmuir adsorption isotherm equation, however, can be quantitatively expressed as follows [Wang, 2010].

$Qe= Qmb* Ce / (1+b Ce)$

Equation 2

Where:

Ce: equipoise concentricity of the dye (mg/L).

Qe: Adsorption capacity (mg/g).

b: stable of the Langmuir adsorption (L/mg).

QM: Langmuir maximum uptake of the two dyes (mg/g).

The Freundlich adsorption isotherm shows that a multilayer of molecules is formed when a solute is adsorbed onto the heterogeneous surface of a solid adsorbent. The Freundlich adsorption isotherm equation can be represented numerically in the manner described [Dada, 2012].

$Qe= KfCe (1/n)$

Equation 3

Where:

Kf: stationary of Freundlich isotherm (L/g).

N: intensity of adsorption.

Langmuir and Freundlich adsorption isotherm equations were expressed in linear forms, respectively, as follows:

The experimental data for the adsorption of methylene_ blue on prepared chitosan were correlated with the linearized form of Langmuir and Freundlich adsorption equations and are shown in Figure (4).

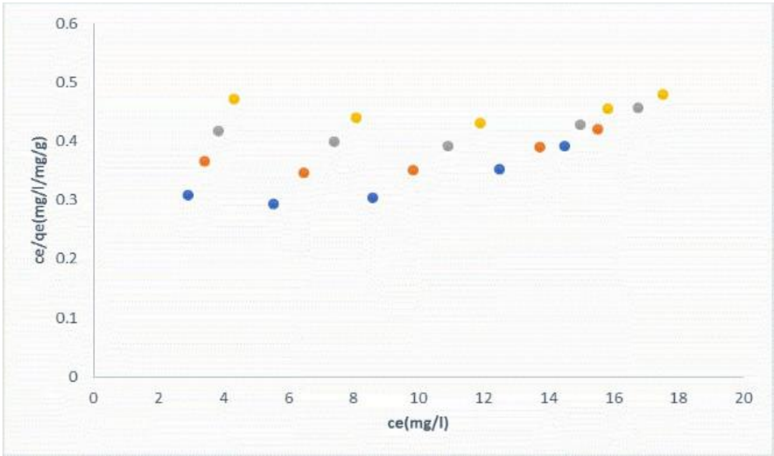

Figure 4. The linearized form of the Fruendlich isotherm paradigm for methylene blue adsorbed on chitosan at various temperatures.

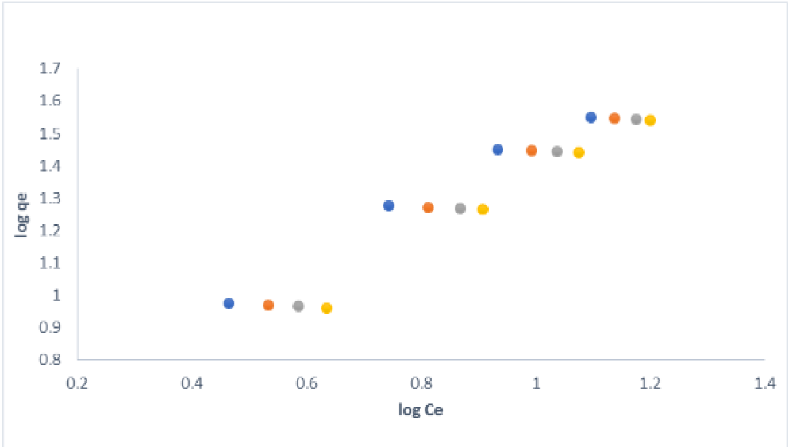

Figure 5. The linearized form of Langmuir isotherm paradigm for methylene_blue adsorbed on chitosan at various temperatures.

These graphs show that the experimental results closely match the Freundlich isotherms. This result indicates that the experimental adsorption of methylene blue on chitosan occurred on a diversified surface and was also a result of the higher focus used in the current study. By observing the values of the confidence level (R2), this unity with Freundlich isotherms can be clearly shown. Table (3) compares equilibrium adsorption data for methylene blue using Langmuir and Freundlich isotherms.

Table 3. Isotherm parameters for methylene blue at heat domain (25-40) ◦C

Temp. ◦C	Langmuir model			Freundlich model		
	Qm (mg/g)	b (l/mg)	R^2	Kf	n	R^2
25	209	0.0171	0.752	-0.0344	1.76944	0.9877
30	426	0.0068	0.5778	-0.0133	2.14350	0.9928
35	1160	0.0021	0.3997	-0.0017	2.55057	0.9953
40	-628	-0.0034	0.0218	-0.0177	3.2498	0.9968

3.2 The impact of the starting concentration

An essential instrument in investigating adsorption capacity is the dye's starting concentration. Additionally, the amount of paint that was removed [Zhang, 2012]. Was determined using the equation shown below): Eq [Wang, 2010].

%removal = (co-ce)/co*100

Equation 4

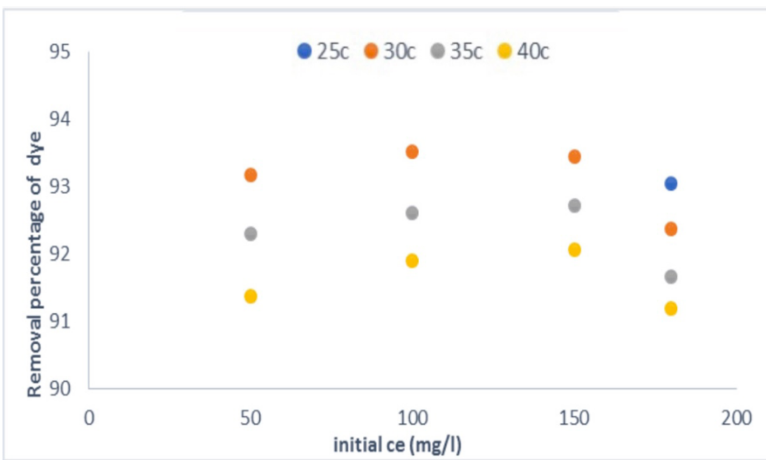

Figure 6. Premier concentricity of methylene blue dye in solution, as a function of removal ratio, from the top, bootstrap, and bootstraps of the chitosan surface. At a temperature (25-40) °C and concentrations of (50 -200 ppm) and contact time 1 hrs.

The initial concentration of methylene blue dye in the solution is plotted against the quantity adsorbed by chitosan in Fig. 6. It was very clear from the graph that the decrease in the removal percentage was related to a rise in the premier tincture concentricity in the solution. While the dye removal rate decreases with increasing premier concentricity, the absorption capacity improves. Figure 6 shows that the clearance percentage of methylene blue at 25 °C decreased from 94.76% to 91.94%, which indicates that. This trend is holding, as research by Suneeta Kumari from 2016 claims. The reason for this behaviour is as follows: Low dye concentrations in liquids sometimes result in a higher initial dye molecule to accessible surface area ratio. Therefore, partial adsorption is not affected by the premier. Even though when dyes are present in solutions in high concentrations, the adsorption sites become less available as they have reached saturation, figure 6 shows a desirable level of initial engagement of each dye in the solution. Up to this point, the correlation between the removal ratio and the starting concentration is practically horizontal, with an optimal value of around 100 mg/L. Contrary to this result, it is possible to remove several colours from aqueous solutions efficiently. They concluded that methylene blue (50 to 200 ppm) was eliminated across the plate.

3.3 The effect of temperature

It is essential to understand how temperature affects the ability of adsorbents to absorb substances during the adsorption process [Corda, 2018]. In Figure 3, the effect of heat on the power of chitosan to bind methylene-blue dye in aqueous solution is shown. The heat domain for the adsorption operation was determined to be (25-40) °C in light of the expected values for the industrial process. These data unequivocally demonstrate that higher temperature reduces the dye's ability to adhere to surfaces. This finding is consistent with a previous [Yagub, 2014a].In addition, since the process is exothermic, the adsorption capacity decreases with increasing temperature. This behaviour may be due to the reduction of the attractive forces that exist, with increasing temperature, between the dye molecules and the active sites on the surface of the adsorbent. The effect of heat on the proportion of pigments removed is shown in Figure 6. These results show that the amount of dye extracted from the surfaces reduces the temperature rise. The clearance of methylene blue decreased from 94.76% to 90.97% during the heat increase from 25 °C to 40 °C. They point out that as the temperature rises, the adsorption forces between the dye molecules and the active sites weaken, decreasing the effectiveness of dye removal.

4 KINETIC OF ADSORPTION

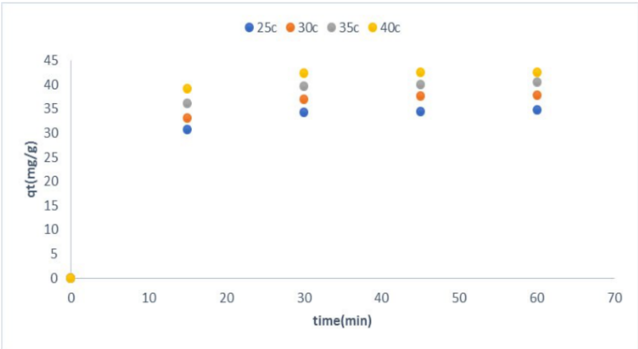

Figure 7. Average of adsorption for methylene blue on chitosan at different temperatures

In Figure 7, the amount of methylene blue adsorbed on the generated chitosan is shown as a function of time and heat (25–40 °C). These data demonstrate that the amount of both adsorbed dyes increases significantly at the first forty minutes; after that (when reaching the equilibrium), it doesn't change any more. The rate of dye adsorption on chitosan decreases over time, with a rapid initial uptake followed by a gradual decrease until it reaches equilibrium. It may be attributed to the diminishing driving force of adsorption, which is the difference between the concentration of the dye in solution and the concentration of the stain on the surface of the adsorbent. In the present study, the experimental adsorption data were analysed using different kinetics models, including the pseudo-first-order and pseudo-second-order kinetics adsorption models in eq (5, 6). These models provide mathematical representations to describe the adsorption process and its kinetics.

$$\textbf{1st order} \quad dqt \,/\, dt = K1 * (qe - q)$$

Equation 5

$$\textbf{2nd order} \quad t/\, dt = K2 * (qe - q)2$$

Equation 6

Where:

qt represents the adsorption capacity at time t and is measured in mg/g (milligrams per gram).

K1 is the rate constant of the pseudo-first-order kinetic model and is measured in litters per minute (L/min).

K2 is the rate constant of the pseudo-second-order kinetic model and is measured in g/mg. Min (grams per milligram per minute). The formulas below were created by combining the adsorption kinetic models mentioned:

Figures 8 and 9 illustrate the application of linear equations, specifically the pseudo-first-order and pseudo-second-order models, in fitting interim data about the adsorption process of methylene blue dye on chitosan. The statistical analysis indicates that the experimental data about the adsorption rate exhibits a significant deviation from the expected behaviour described by the pseudo-first-order model. It is essential to acknowledge that the second-order kinetic model effectively describes the experimental data about the adsorption rate.

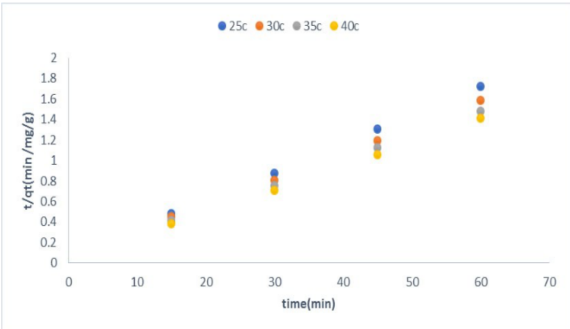

Figure 8. Pseudo-first-order kinetic model for adsorption of methylene_blue on chitosan at various temperatures.

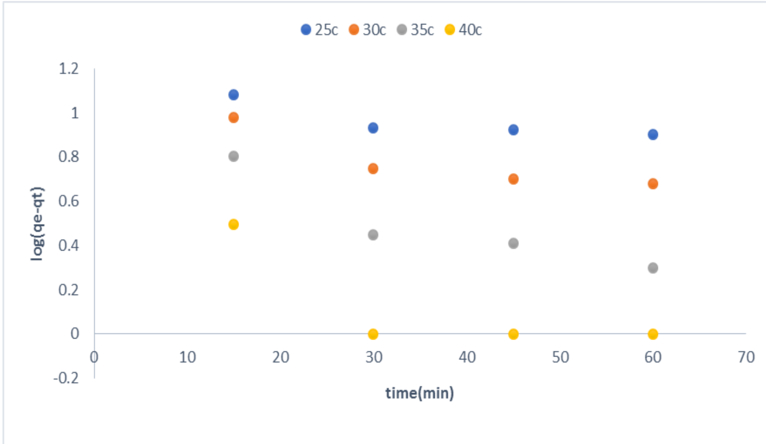

Figure 9. Pseudo-second-order kinetic model for adsorption of methylene_blue on chitosan at various temperatures

Additionally, it may be demonstrated that the pseudo-second-order kinetic model faithfully reproduces the experimental data by looking at the confidence level (R2) for the selected equations. Tables (4 and 5) illustrate the kinetic parameters and the confidence level (R2) for the kinetics model equation by contrasting them with the experimental findings. The tables show that the confidence level for a pseudo-second-order kinetic model is 0.999. Simultaneously, the values obtained for the pseudo-first-order kinetic model and the intra-particle kinetic model are 0.8061 and 0.7844, respectively. This observation showcases the effectiveness of the pseudo-second-order kinetic model in accurately representing the experimental findings.

Table 4. Pseudo-first-order characteristics of the methylene blue adsorption process at various temperatures

Temp. ◦C	Methylene blue		
	qe cal. (mg/g)	k1 (1/min)	R^2
25	2.0786	0.0083	0.7407
30	1.8333	0.0146	0.7877
35	1.6233	0.0238	0.8463
40	1.611	0.0214	0.612

Table 5. Pseudo-second order characteristics of the methylene blue adsorption process at various temperatures.

Temp. ◦C	Methylene blue		
	qe cal. (mg/g)	k2 (g/mg. min)	R^2
25	36.145	0.0126	0.9997
30	39.705	0.0095	0.9996
35	42.035	0.0108	0.9998
40	43.60531	0.0175	0.9996

His outcome is consistent with previously published research [Narayanan, Govindasamy, 2017]. The experimental data for methylene blue elimination from wastewater was represented using pseudo-first-order, pseudo-second-order, and inter-particle diffusion kinetic models. They concluded that the experimental data are well-fit by the second-order kinetic model, with a confidence level of R2 = 0.999.

5 CONCLUSION

Based on the findings of this study, it is evident that chitosan powder exhibits notable efficacy and efficiency as an adsorbent in removing methylene blue dye from wastewater originating from industrial sources. The observed removal effectiveness of 94% at a temperature of 25 °C suggests that chitosan possesses a significant potential for removing dye impurities. Using chitosan as a therapeutic approach offers notable economic advantages due to its abundant availability and cost-effectiveness. The sustainability and environmental friendliness of this material are enhanced by its derivation from marine shell debris. Hence, the utilisation of chitosan as a potential remedy for the treatment of industrial wastewater contaminated with dyes is a promising and economically feasible approach.

Furthermore, the research yielded valuable findings regarding the kinetics and equilibrium characteristics of the chitosan absorption mechanism. The findings above have the potential to enhance therapeutic effectiveness and aid in the identification of suitable circumstances for the application of chitosan. The results of this research can provide a foundation for future investigations centred on the remediation of industrial wastewater contaminated with a dye. The utilisation of chitosan has the potential to make a positive impact on environmental preservation by effectively addressing the detrimental consequences posed by dye pollution on human health and marine ecosystems. Based on the findings above, it is recommended that more investigation be undertaken to enhance and advance the utilisation of applications across diverse sectors. The results from equilibrium studies suggest that the adsorption of methylene blue dye by chitosan powder takes place within the initial thirty-minute period of the adsorption process. Chitosan exhibits a very efficient and expeditious adsorption mechanism, rendering it a remarkably efficacious substance for eliminating dye pollutants from industrial effluent.

Additionally, the study observes that the adsorption process adheres to Freundlich's law, which characterises the heterogeneous properties of the adsorption surface. This finding suggests that the ability of chitosan to absorb dyes is not consistent across different concentrations, hence enabling the efficient treatment of a broader range of dye concentrations. The study observed that the Freundlich model had superior fitting capabilities to the Langmuir model. This outcome suggests that the Freundlich model offers a more precise depiction of the adsorption mechanism of methylene blue on chitosan, as supported by the experimental data. The second-order model exhibited superior suitability in the field of kinetics compared to the first-order model, as evidenced by a substantial coefficient of determination (R2) of 0.999. The author proposes that the adsorption process adheres to a chemisorption mechanism, implying a robust chemical contact between dye molecules and the chitosan surface. These findings provide more evidence to substantiate the efficacy and cost-effectiveness of chitosan as a viable adsorbent for removing dye pollutants from industrial wastewater. A comprehensive comprehension of the equilibrium and kinetic characteristics of the adsorption process is of paramount importance to enhance processing methodologies and promote the effective utilisation of chitosan across diverse industrial sectors.

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