

Original Research

Chitin Beads from *Peneaus* sp. Shells as a Biosorbent for Methylene Blue Dye Removal

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Received: 8 December 2017

Accepted: 23 April 2018

Abstract

The adsorption potential of chitin, a polysaccharide found in the exoskeleton of shrimp, was evaluated using methylene blue cationic dye. Batch adsorption studies were done using a column by optimized bed height of 22.2 cm and retention time of 90 min. The alginate:chitin ratio was taken as 1:07 with 80 mg/l-initial dye concentration, and pH was maintained at 8. There was 90% adsorption of dye. Langmuir and Freundlich isotherms were studied along with the adsorption kinetics. The plots indicated that the data fitted Langmuir isotherm. The R^2 is greater for pseudo second-order kinetics and Weber and Morris' model on intra particle diffusion best fit this adsorption by chitin.

Keywords: adsorption, chitin, isotherms, kinetics, methylene blue

Introduction

The textile and leather industries require dyes to impart colour to many products, but dye effluents from these industries have hazardous environmental effects. More than 100,000 commercial dyes are available to the textile industries worldwide. 10-25% of textile dyes are lost during the dyeing process and around 20% effluents mix with various environmental components, causing harm if they are not treated properly. The double bonds and aromatic rings in the chemical structure of dyes are difficult to degrade because it can resist heat up to 300°C [1].

Methylene blue, a cationic dye with molecular weight 373.90 g mol⁻¹, is commonly used in the textile and leather industries. In humans, methylene blue may

cause hazardous effects like tachycardia, nausea, blue coloration of skin, and death of premature cells in the tissues [2]. Adsorption is the best process for textile dye effluent treatment. It commonly uses activated carbon as an adsorbent but it cannot be used in industries because of its expensive operational costs and low regeneration capacity. Hence, there is rigorous research for developing a cheap material as adsorbents of these textile dyes. Bio-sorbents like marine plants, humus, moss peat, modified cotton, chitin, and chitosan are alternating resources used for exclusion of toxic effluents from industries [3].

Chitin is a naturally abundant and renewable polymer as it is degradable, bio compactable, and a nontoxic adsorbent. Chitin structure has β -(1-4)-2-acetamido-2-deoxy- β -D-glucose [4], wherein C-2 position has acetamide groups (Fig. 1). Commercial shells of arthropods (exoskeletons) are the major source from which chitin is obtained – especially of crabs and shrimp [5].

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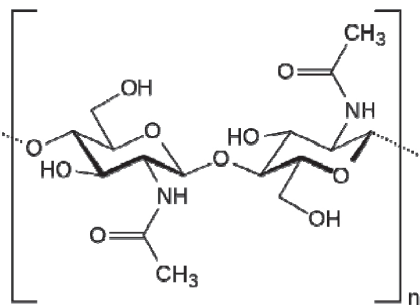


Fig. 1. Chitin structure.

This study was done to adsorb methylene blue dye using chitin obtained from shrimp exoskeleton wastes, and also to study isotherm and kinetic models to determine the favourable method of adsorption. There is a waste-to-wealth approach in this system of study as procuring the raw material chitin is inexpensive since it is a waste product of seafood export industries.

Materials and Methods

Preparation of Adsorbent

One percent sodium alginate (Hi-Media) was prepared by warming it continuously in distilled water for the alginate to get dissolved completely. This was followed by the addition of 2 g of chitin (Hi-Media) powder with continuous stirring. The chitin-alginate mixture was then added as droplets in 5% calcium chloride solution using a sterile dropper.

Methylene Blue Standard Preparation

Methylene blue stock (Hi-Media) of 100 mg l⁻¹ was prepared, and this solution was used for the standardization process. A UV-visible spectrophotometer reading was taken at 660 nm, (Perkin Elmer, Lambda 25, USA) and this stock solution was used for further optimization experiments.

Optimization of Dye Adsorption

The retention time was optimized by packing 115 g of chitin beads to a bed height of 22.2 cm in a 42 cm column (37 cm working column + 5 cm head space; bed height:column height = 0.6). Dye stock solution was fed into the column, and the system was kept undisturbed. After 10 min the sample was eluted, and absorbance was read at 660 nm. The experiment was repeated for every 20 min till 120 min. Similarly, optimal adsorption efficiency was determined by varying bed height (7.4 cm, 11.1 cm, 14.8 cm, 18.5 cm, and 22.2 cm), pH (4 to 10), alginate:chitin ratio (1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, and 1:9), and dye concentration (20 mg l⁻¹ to 100 mg l⁻¹). Removal efficiency of chitin is:

$$\text{Removal efficiency} = [(C_0 - C_t)/C_0] * 100$$

...where C_0 is the initial concentration of methylene blue and C_t is the solution concentration after adsorption at any time [6].

Isotherms of Chitin Methylene Blue Adsorption

Langmuir [7] established batch adsorption isotherm for surface adsorption relating the concentration of adsorbate initially and after adsorption, which is expressed as:

$$C_e/Q_e = C_e/Q_m + 1/Q_m b$$

...where C_e is the equilibrium concentration of dye in solution (mg l⁻¹), Q_e is the amount of dye adsorbed on the adsorbent at equilibrium (mg g⁻¹), Q_m is the monolayer adsorption capacity (mg g⁻¹), and b is the Langmuir constant (l mg⁻¹)[8]:

$$Q_e = (C_0 - C_e) V/m$$

...where C_0 and C_e (mg l⁻¹) are the liquid-phase residual concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (l) and W is the mass of dry sorbent used (g) [9].

Separation factor R_L [10] was used to test the validity of Langmuir isotherm and was calculated as follows:

$$R_L = 1/(1 + bC_0)$$

...where C_0 is the initial concentration of dye and b is the Langmuir constant [8].

Freundlich isotherm [11] for this process is:

$$\text{Log } Q_e = \text{Log } K_f + 1/n \text{ Log } C_e$$

K_f and n are constants [8].

Adsorption Kinetics

The dye adsorption kinetic and intra particle diffusion study on chitin beads was done [12-14].

FTIR of Chitin Beads

Fourier transform infrared (FTIR) characterization of chitin and methylene blue was done. KBr disks of chitin beads were prepared and the functional groups present were graphically identified using an ASCII PEDS 1.60 FTIR spectroscope in the range of 4000 to 400 cm⁻¹.

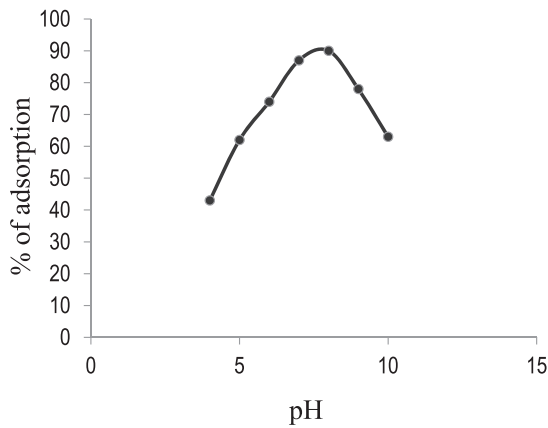


Fig. 2. Chitin beads adsorbing methylene blue dye at different pH.

Results and Discussion

Chitin Beads Adsorbing Dye at Different Initial pH

Fig. 2 shows the trend of dye adsorption with varying pH that contributes to the ionization of chitin and methylene blue. There was 90% maximum adsorption at pH 8 [15] for the dye concentration of 80 mg^l⁻¹, and this was considered the optimal level for further experiments. The cations are adsorbed at pH > pHzpc of chitin, while anions are adsorbed at pH < pHzpc of chitin, and pHzpc of chitin was found to be 6 [16]. It has also been reported by Dotto et al. [17] that at higher pH, negatively charged deprotonated chitin have attractive electrostatic interaction with positively charged methylene blue dye. From pH 4 to 8 there was an increase in adsorption, but it decreased with further pH increase. This is because the decrease in negatively charged sites on the chitin beads (increased cationic dye molecules), thereby resulting in electrostatic repulsion [18]. Alzaydien et al. [19] and Saed et al. [20] stated that the concentration of H⁺ ions determines the adsorption and also obtained similar results.

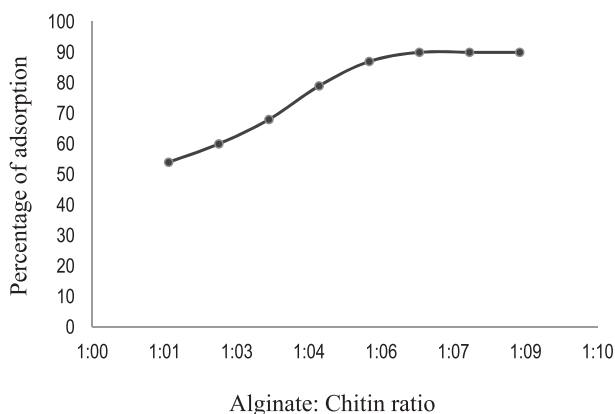


Fig. 3. Chitin beads adsorbing methylene blue dye; different ratios of alginate:chitin.

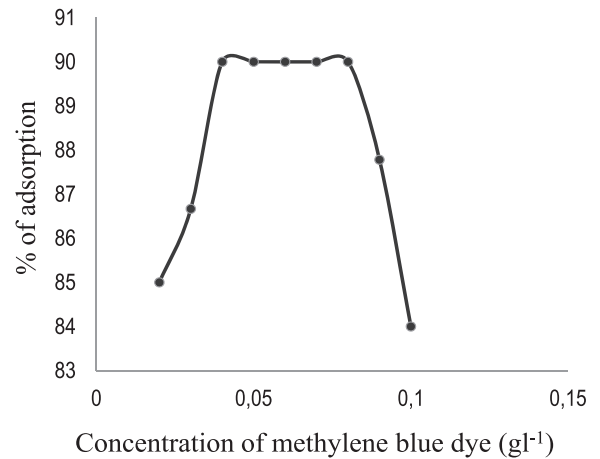


Fig. 4. Chitin beads adsorbing methylene blue dye at different dye concentrations.

Different Dosage Ratios of Alginate:Chitin

A plot of alginate:chitin ratios and adsorption percentages are shown in Fig. 3, and 1:07 ratio of alginate:chitin was identified as optimum ratio. There was no further adsorption with increased concentration of chitin. Jeyavathana et al. [21] suggested that decreased particle size and increased chitin dosage is a driving force for adsorbate that goes deep inside the pores to bind to the chitin. In a study by Unal et al. [22] using waste *Elaeagnus* stone, the adsorption increased with the increase in concentration of dosage, but the optimum level was comparatively lower than chitin:alginate.

Chitin Beads Adsorbing Dye at Different Dye Concentrations

90% adsorption was observed (Fig. 4) at 40 mg^l⁻¹, remained the same until 80 mg^l⁻¹, and started decreasing at 100 mg^l⁻¹. To make the process efficient, a higher dye concentration of 80 mg^l⁻¹ was considered optimal. Jirekar et al. [23] used 100 mg^l⁻¹ of green gram obtaining only 79.85% adsorption and Rahman et al. [24] using 4 mg^l⁻¹ on rice husk obtained around 70% adsorption only, although EI-Waki et al. [25] reported around 95 to 98% with activated carbon from papyrus plant treated with chemicals. Initially the adsorbent has many unoccupied active sites, hence adsorption increases. After maximum adsorption capacity is reached the binding sites become unavailable and there is no further change in adsorption [5].

Chitin Beads Adsorbing Dye at Regular Interval of Time

Chitin beads adsorbing methylene blue dye at different time intervals is graphically represented in Fig. 5. As the retention time of the dye increased,

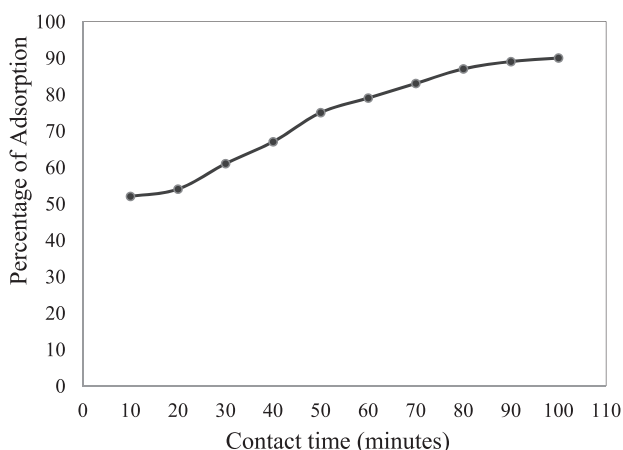


Fig. 5. Chitin beads adsorbing methylene blue dye at regular time intervals.

the percentage of adsorption increased. At 90 min, a maximum adsorption of 90% of dye was observed and it remained the same further during the process. The adsorption process occurs in three steps, namely boundary layer diffusion, surface adsorption, and pore diffusion. Hence, it takes a longer time for optimal adsorption to take place [26]. Shehata [8] also stated that the adsorption process took reasonably long retention time due to the three steps in adsorption, and the maximum absorption at 90 min using animal bone was obtained. El-Maghraby and El Deeb [27] used rice hulls and obtained maximum methylene blue adsorption at 90 min. Activated carbon from shells of *Pongamia Pinnata* seeds also showed similar results with a faster rate of adsorption initially [28].

Chitin Beads Packing at Different Bed Heights

The adsorption percentage of dye by chitin beads increases as the bed height increases, which is shown in Fig. 6. At 22.2 cm there was a maximum adsorption of 90% (working volume:reactor volume = 0.6). Timi Tarawou et al. [29] also proved that as the height increases, 100% adsorption of the dye is possible but the

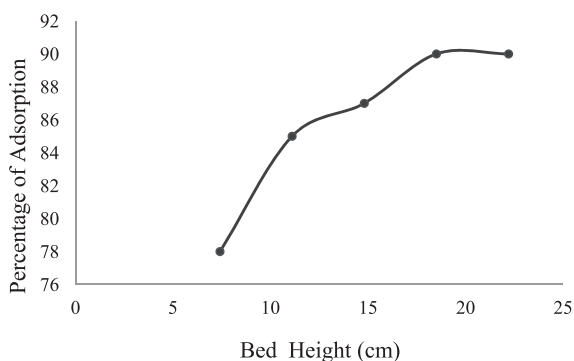


Fig. 6. Chitin beads adsorbing methylene blue dye; chitin bead packing at different bed heights.

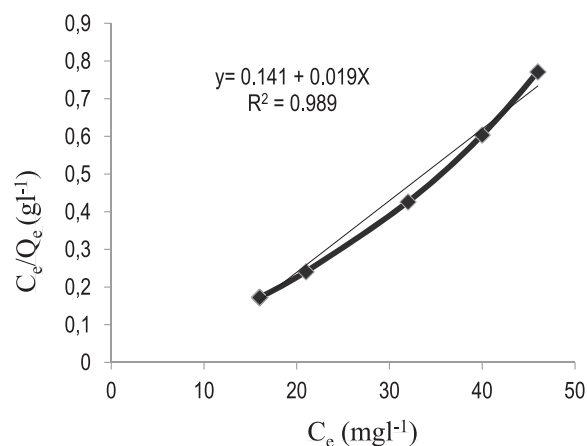


Fig. 7. Chitin beads adsorbing methylene blue dye; Langmuir isotherm for dye adsorption.

time taken for the process also increases. Jabbar et al. [30] used a granulated activated carbon bed at different heights and obtained maximum adsorption as the height increased because of the availability of plenty of surface area and time for reaching saturation level.

Isotherms for Dye Adsorption

A plot for methylene blue dye Langmuir isotherm is shown in Fig. 7. C_e/Q_e was plotted against C_e , the amount of dye adsorbed onto beads, and at varied concentration of the adsorbent a linear plot was obtained. The adsorption process fits Langmuir isotherm when $0 < R^2 < 1$ and preferably when $R^2 > 0.98$ [31]. Table 1 reveals that $R^2 = 0.98$, and it fitted the Langmuir isotherm and also that the process was favourable.

Further confirmation of the process feasibility can be analysed by separation factor, R_L . Fig. 8 shows variation of R_L with the quantity of methylene blue adsorbed at varying chitin concentrations (C_e). Adsorption

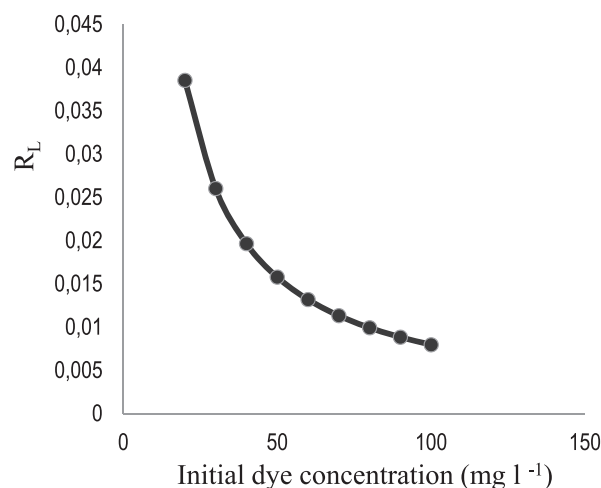


Fig. 8. Chitin beads adsorbing methylene blue dye; determining separation factor from Langmuir isotherm for dye adsorption.

Table 1. Chitin beads adsorbing methylene blue dye; implications of adsorption isotherms.

Types of isotherm	Favourable conditions	Q_m ($mg\ g^{-1}$)	b ($l\ mg^{-1}$)	K_f ($mg\ g^{-1}$)	n	R^2
Langmuir isotherm	$0 < R^2 < 1$ R^2 close to 1	52.63	0.13	-	-	0.989
Freundlich isotherm	$1 < n < 10$ R^2 close to 1	-	-	3.10	2	0.974

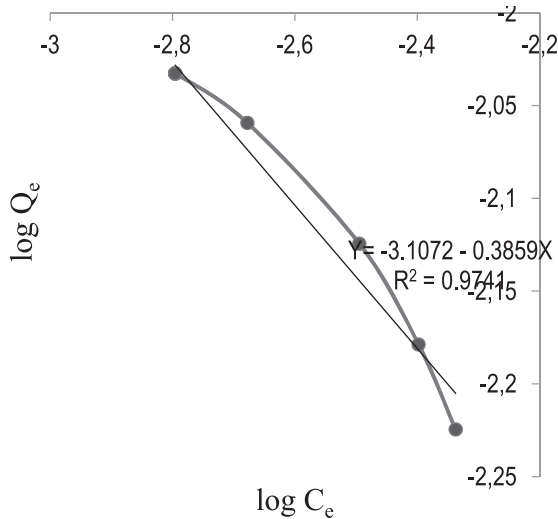


Fig. 9. Chitin beads adsorbing methylene blue dye; Freundlich isotherm for dye adsorption.

is considered favourable when $0 < R_L < 1$, linear if $R_L = 1$, and irreversible if $R_L = 0$ [32]. It is proved to be favourable with the experimental data from Table 1. $R^2 = 0.974$ and $n = 2$ was obtained from a graph of $\ln Q_e$ vs. $\ln C_e$ plotted for Freundlich isotherm (Fig. 9). It was comparatively lesser than the R^2 value obtained in the Langmuir isotherm. Muhammad [33] reported favourable adsorption conditions when the value of 'n' between 2-10, inconvenient for $n = 1-2$ and unsuitable for $n < 1$. R^2 value and adsorption capacity from the Langmuir isotherm were better than those obtained from the Freundlich isotherm.

Experimentally there is homogeneous, uniform adsorption due to equal activation energy for both methylene blue and chitin, hence fitting Langmuir's model. Similar results favouring Langmuir isotherm were observed by Neerajet et al. [34] using coal fly ash, Yu-Shan Hoet et al. [35] with *Delonix regia* pods, and Daniele et al. [36] from plant litters.

Kinetics of Dye Adsorption

Fig. 10(a-b) is a plot for chitin and methylene blue kinetics, and Table 2 represents its R^2 , K_1 , and K_2 values. From the graph it is inferred that adsorption data fits pseudo second-order kinetics as R^2 value was high, which also was reported by Huayueet et al.

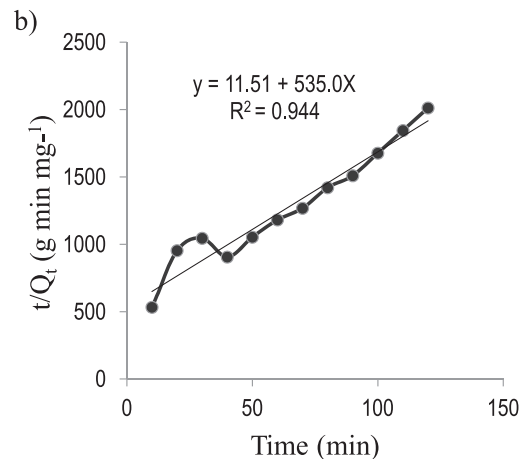
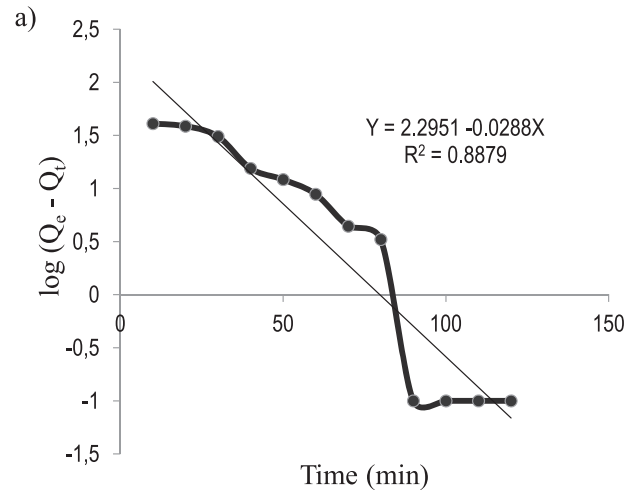


Fig. 10 a) Chitin beads adsorbing methylene blue dye; pseudo first-order kinetics of dye adsorption; b) Chitin beads adsorbing methylene blue dye; pseudo second-order kinetics of dye adsorption.

[37] using chitosan as adsorbent for carcinogenic dye similarly.

A graphical representation of Q_t vs. $t^{0.5}$ is shown in Fig. 11, indicating intraparticle diffusion model, and the parameters obtained from the plot are shown in Table 2. The intercept was not zero – clearly indicating a boundary layer effect and intra particle diffusion is the rate-limiting step [38]. Linearity in the graph shows that intraparticle diffusion of dye had taken place and its slope gives rate constant of diffusion. A decline in the intra particle diffusion takes place once the process reaches equilibrium level.

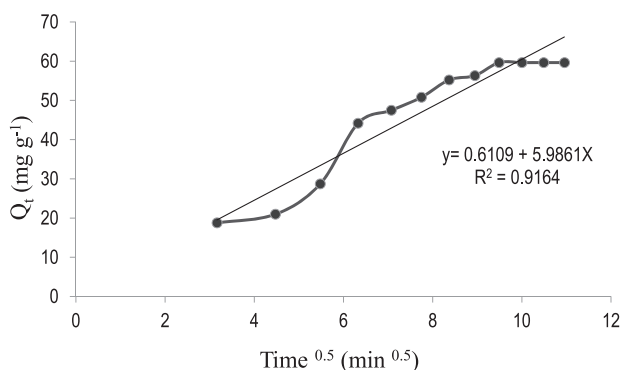


Fig. 11. Chitin beads adsorbing methylene blue dye; intra particle diffusion kinetics of dye adsorption.

Table 2. Chitin beads adsorbing methylene blue dye; kinetics of dye adsorption.

Types of kinetic models	Rate constant	Correlation coefficient
Pseudo first-order	$K_1 = 0.012 \text{ min}^{-1}$	0.88
Pseudo second-order	$K_2 = 535 \text{ min}^{-1}$	0.94
Intra-particle diffusion $t^{0.5} = 4.15 \text{ min}$ $C = 0.61$	$K_{id} = 5.98 \text{ mg g}^{-1} \text{ min}^{-1}$	0.91

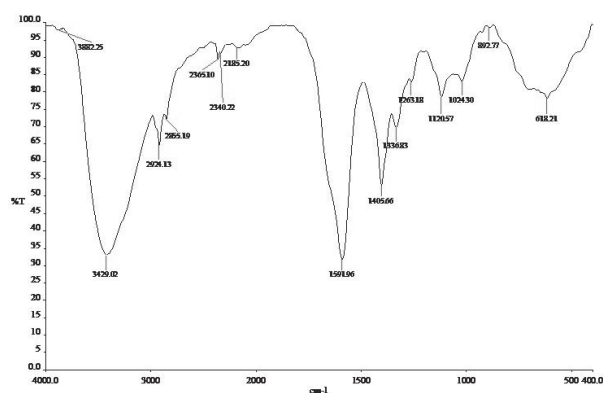


Fig. 12. FTIR of chitin.

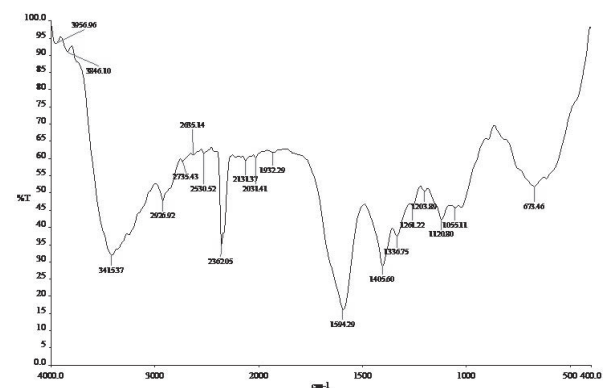


Fig. 13. FTIR of chitin-methylene blue.

FTIR Analysis

FTIR spectra were analysed for chitin initially and along with methylene blue (Figs 12-13). The β -glycosidic linkage in the chitin polymer is inferred from the peak at 1120 cm^{-1} . Hydroxyl groups of the carbohydrate are responsible for the broad and strong adsorption around 3429 cm^{-1} . Moreover, the vibrations were observed at 2924 cm^{-1} for aliphatic C-H stretching as well as 1336 cm^{-1} for C-N stretching, which clearly indicates the structure of chitin.

The aromatic ring vibrations of methylene blue were present at 1405 cm^{-1} and 1594 cm^{-1} . Weak adsorption at 673 cm^{-1} indicated C-S stretching. A confirmation for adsorption is given by aliphatic C-H stretching vibrations at 2926 cm^{-1} and vibrations at 1336 cm^{-1} for C-N stretching.

Conclusion

There was an effective 90% adsorption by chitin after the optimization of various parameters like retention time, pH, etc. The dye adsorption pattern follows pseudo second-order kinetics and also suggests monolayer adsorption as confirmed by Langmuir isotherm. Hence existing chemical adsorbents used in the effluent treatment system in textile industries can be replaced by chitin alginate beads as a highly effectual nontoxic biopolymer.

Conflict of Interest

All the authors declare no conflict of interest.

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