

Bio-adsorption of methylene blue dye using chitosan-extracted from *Fenneropenaeus indicus* shrimp shell waste

Abstract

The cationic dye “Methylene blue” is widely used in textiles industry, pharmaceuticals, paper industries, and ink manufacturing etc. The washed off dyes discharged directly in water bodies and cause major damage to the environment. The molecule of dye is very stable, so that it is very difficult to decompose naturally. Therefore, it is essential to remove the dye by purifying, and prevent the environment from pollution. The $-NH_2$ and $-OH$ functional groups of Chitosan can induce the adsorbing capacity of dyes by its low surface area, porosity and high crystalline nature. Chitosan is an environment friendly, non-toxic, easily available, biodegradable, renewable biopolymer, and harmless to biota. Extraction of chitosan from the “*Fenneropenaeus indicus*” (Shrimp) shell and its utilization in wastewater treatment controls the environmental problems and contributes to solid waste management. In this study, the possible use of “*Fenneropenaeus indicus*” (Shrimp) shell chitosan for the bio-adsorption of MB dye was investigated by a batch adsorption method using different adsorbent doses with respect to experimental duration. The maximum amount of dye adsorption was obtained at a minimum dose of 4gram chitosan, with experimental time of 4 hours. The *Fenneropenaeus indicus* shell chitosan was found to be a better adsorbent since it removes about 93.23% of methylene blue dye from sample water. Further, characterization of functional groups was also done and the changes of groups were observed from both control and treated samples.

Keywords: *fenneropenaeus indicus*, methylene blue dye, chitosan, ft-ir, functional group

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Introduction

The fast development of the industrial sector leads to releasing a higher quantity of dye waste-water directly into the natural environment, which causes direct effects in human health.¹ The cationic dye Methylene blue is widely used in textiles industry, pharmaceuticals, paper industries, and ink manufacturing etc.,² The molecule of dye is very stable, so that it is very difficult to decompose naturally. Therefore, it is essential to remove the dye by purifying, and prevent the environment from pollution.³ The polluted water contains a higher concentration of Chemical Oxygen Demand and Biochemical Oxygen Demand; and large quantities of suspended solids etc. Hence critical techniques are essential in the treatment of discharged wastewater. Chemical methods, coagulation, flocculation, reverse osmosis, Nano-filtration, Ultra-filtration methods are commonly in use. But, these techniques are very complex and cost effective. Since developing countries are not convenient with these techniques for removal of dyes from textiles industries, the adsorption method was considered as the best solution for removal of industrial dyes from discharged water.⁴

During the past few years, much concentration has been given to the discovery and preparation of adsorbents to remove various pollutants from industrial discharge, in consideration with advantages such as efficiency, low cost, eco friendly, biodegradable, renewable biopolymer.⁵ Adsorption is the surface phenomenon in which the dye gets attached to the adsorbent's surface. Testing of bio-adsorbents is a big task for environmentalists and engineers with respect to its potential.⁶ The production of shrimp waste is an alarming problem in sea food exporting nations like India.⁷ Extraction of shrimp shell chitosan and its usage in treatment of wastewater is an additional

income source. It also reduces the disposal problem of shrimp waste by solid waste management.⁸ The $-NH_2$ and $-OH$ functional groups of Chitosan can induce the adsorbing capacity of dyes.⁹ Chitin & chitosan was commonly used in removal of dyes.¹⁰ Researchers have concentrated on the use of chitin/chitosan-containing residues from crustacean shells without any modification, and compared the results with pure flakes of chitin and chitosan.¹¹ Therefore, the present study was conducted to adsorb the Methylene Blue (MB) using Chitosan extracted from *Fenneropenaeus indicus* shrimp shell waste.

Materials and methods

Collection of shrimp shell waste and pre-processing

Fresh shells of *Fenneropenaeus indicus* were obtained from Kasimedu local fish processing center-Royapuram, Chennai. The collected raw shells of shrimp were rinsed thoroughly with tap water to flush off debris and unwanted tissues. Further, the samples were dried at 55°C in a hot air oven. After drying, the shrimp shell materials were ground into small pieces to obtain a uniform size product using pestle and mortar and kept in a closed moist free container for future use.

Extraction of chitin and chitosan

The chitin & chitosan extraction were done followed by Tarafdar and Biswas¹² method with some modification.

Chemicals and reagents were used

NaOH (Sodium Hydroxide)

HCl (1 M Hydrochloric acid)

Deproteinization: Grinded shrimp shell (50g) is taken in a conical flask containing 10g of (4%) sodium hydroxide added with 250ml of distilled water in it. It is then incubated for 24 hours at $28^{\circ}\text{C} \pm 3^{\circ}\text{C}$. The alkali liquid was filtered out and the filtrate collected separately in a conical flask. Further the sample was rinsed repeatedly with distilled water until pH come to 7.2 ± 0.2 approximately neutral (Figure 1).



Figure 1 Chitin.

Demineralization: To the remaining filtrate in the conical flask, 4% (1M) hydrochloric acid was added (1:5; w/v) and incubated at $28^{\circ}\text{C} \pm 3^{\circ}\text{C}$ for 24 hrs. The liquid was filtered out and the solid filtrate was collected separately. Further, filtrate was washed many times with distilled water until the pH comes to 7.2 ± 0.2 approximately and dried in hot air oven at 55°C . The extracted chitin was weighted and the yield (%) was calculated as;

$$\frac{\text{Final dry weight of prawn shell}}{\text{Initial dry weight of prawn shell}} \times 100$$

Deacetylation: Chitin flakes in the conical flask were added with 50 % sodium hydroxide solution (1:5; w/v). It was incubated at $28^{\circ}\text{C} \pm 3^{\circ}\text{C}$ for 3 days and then the liquid was filtered and the solid filtrate was collected separately in a conical flask. The filtrate was washed and dried. The dried extract chitosan (Figure 2) was weighed and the yield (%) was calculated as;

$$\frac{\text{Final dry weight of prawn shell}}{\text{Initial dry weight of prawn shell}} \times 100$$



Figure 2 Chitosan.

Biosorption of methylene blue dye using chitosan

The methylene blue dye adsorption using chitosan obtained from *Fenneropenaeus indicus* shrimp shell waste was followed by the method of Rahman and Akter.¹³ A total of 500ml of 10ppm stock solution of methylene blue reactive dye was made up by dissolving 5mg of methylene blue dye in 500ml of distilled water (Figure 3). The adsorption isotherm was carried out using prepared solution.



Figure 3 Stock solution of Methylene Blue dye.

Batch adsorption experiment was carried out in 4 experimental glass beakers, each filled with 50ml of prepared dye sample and mixed with chitosan with different amounts (1g, 2g, 3g & 4g respectively) at $28^{\circ}\text{C} \pm 3^{\circ}\text{C}$. The mixture was stirred well until the mixture was left to settle.

Experiment 1:

The effect of time period: In this experiment, effect of contact time between adsorbent and adsorbate were studied from 0 hours to 48 hours for determining the optimum time in which there is complete decolourization of the methylene blue dye.

Experiment 2:

The Effect of adsorbent dose: The experiment for the observation of adsorbent dose effect was carried by adding 1g to 4g of adsorbent for 50ml solutions in 4 experimental glass beakers respectively for determining the optimum adsorbent amount in which there is complete decolourization of methylene blue dye.

Experiment 3:

UV-Vis absorbance percentage

The adsorption capacity was calculated using UV-Vis spectrophotometer at 665 nm.

Calculation

$$\frac{\text{Absorbance of control} - \text{Absorbance of sample}}{\text{Absorbance of control}} \times 100$$

Chitosan characterization using FT-IR

The characterization of chitosan was determined by using Fourier Transform - InfraRed (FT-IR) spectrophotometer.

Results and discussion

The *Fenneropenaeus indicus* shrimp chitin & chitosan extract was found to be 62% and 45.74% respectively. The adsorption effect of shrimp chitosan on methylene blue was determined by UV-Vis absorbance (665nm) for the colour change in four experimental beakers containing different concentrations of adsorbent (Figure 4). It is evident that 4g of chitosan adsorbent gave optimum result in decolourization of methylene blue dye (Figure 5) with a maximum

adsorbing capacity of 93.23% (Figure 6). The same experiment was conducted upto 48 hours, but complete decolourization of methylene blue was achieved in 4 hours itself and the same level of decolourization remains even after 48 hours. Since the concentration gradient between chitosan and prepared dye material was high, the removal percentage was also high until equilibrium is reached by the system. After the attainment of equilibrium and saturation point, the prepared dye material remains in the solution and the adsorption percentage was decreased.¹⁴

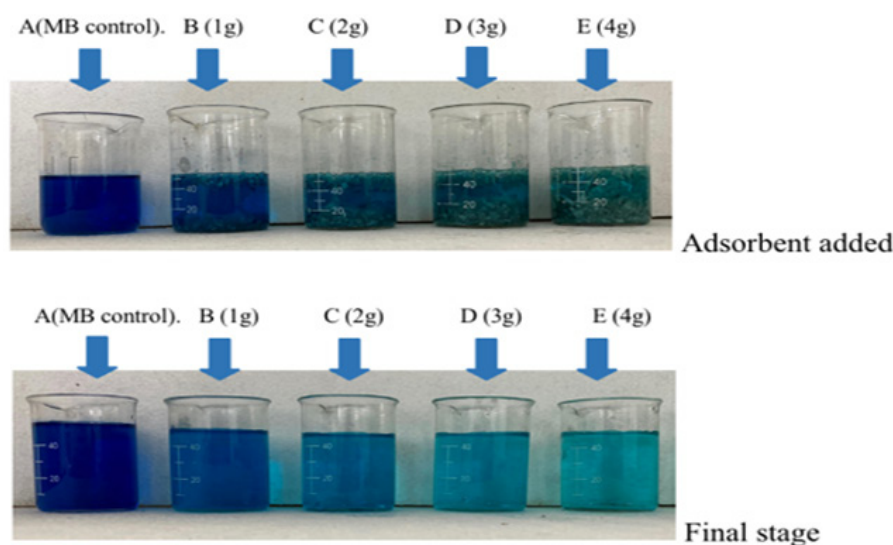


Figure 4 Comparison of Color change Methylene blue dye adsorbed chitosan.

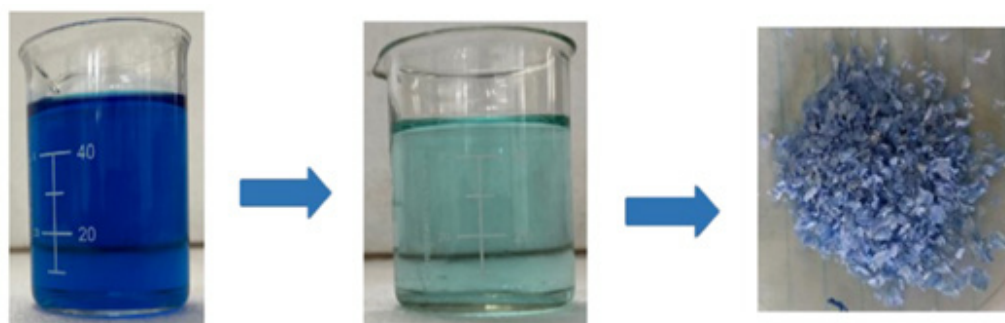


Figure 5 Comparison between untreated and treated water (before & after the experiment).

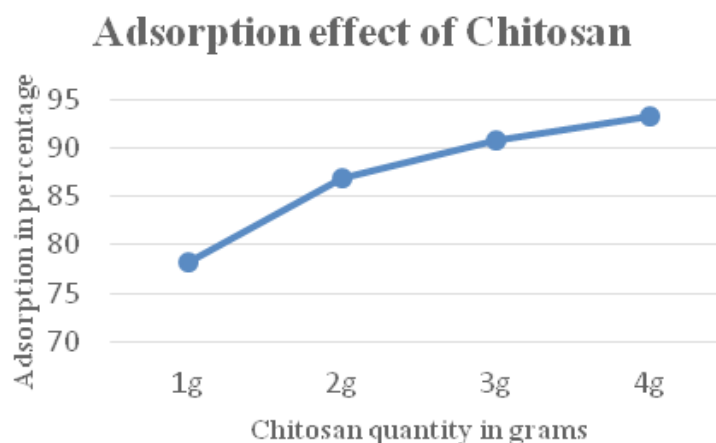


Figure 6 Methylene Blue removal percentage for different amount of chitosan.

The functional groups of chitosan (before and after the treatment) were confirmed using FT-IR spectroscopy (Figure 7). The FT-IR spectrum around 3400/cm shows the occurrence of OH stretching. The wave number 2090/cm indicates the availability of C=C=O, stretching groups in control and treated chitosan, which is the characteristic of chitosan bio polymer. It is absent in Methylene blue spectrum. The stretching of 1640 is present in Methylene blue and Methylene blue adsorbed chitosan, which is absent in chitosan

(control). It indicates the adsorbed methylene blue spectrum in the sample due to the presence of -C=N group. All other stretches such as 1553 (-CO-N), 1380 (-CH₃), 1259 (=C-O), 1008 (-NH₂), 869 (N-H) is present in Chitosan and Methylene blue adsorbed chitosan. This presence of asymmetrical stretching strongly indicates the presence of the chitin derived molecule of chitosan. Many functional groups are shifted and combined with other relative groups due to a rise in concentration gradient between chitosan and methylene blue dye.

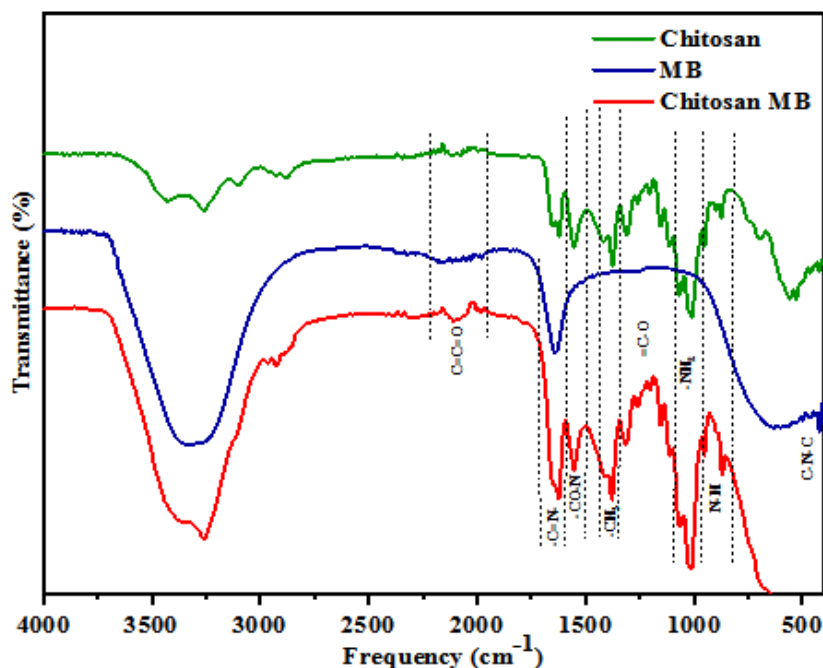


Figure 7 FTIR spectrum comparing Chitosan, Methylene blue and Methylene blue adsorbed-Chitosan.

It is clear evident that there is a gradual increase in decolourization ability of chitosan on methylene blue dye with increasing amounts of adsorbent. The 4g of adsorbent (chitosan) showed maximum decolourizing capacity (93.23%) on the dye. Similarly in general at various amounts of adsorbent (chitosan), the contact time for decolourization was 4 hours.

In this experiment, the quantity of extracted chitin and chitosan from shrimp was lower than the study carried by Kamala et al., and Raja et al.^{15,16} due to inter-species variation of biopolymer content in shells and the extraction procedures. The effective adsorption of methylene blue dye removal from wastewater had resulted in a good substitute for other expensive treatment methods. The work conducted by Rahman and Akter¹³ suggests the possibility of using shrimp shell chitin for the removing methylene blue dye from polluted discharge of textile industries. The removal efficiency of 1.5gram of chitin was almost 96% and the retention duration was 60 min. The bio-adsorbent (Chitosan) has gained popularity in industries for waste water treatment due to its higher content of amine and hydroxyl functional groups than chitin.¹³

The data of Dassanayake results that in 2.5 minutes and at a pH of 7.2±0.2, The presence of Manganese dioxide-chitin mixture (1.0g L⁻¹) decolourises 98% of MB solution (20mg L⁻¹) in 30 seconds and complete decolorization takes place in 2.5 minutes and eight percent of MB solution (20mg L⁻¹) was decolourised by chitin (1.0g L⁻¹). Methylene blue solution which contains Manganese dioxide (1.0g L⁻¹) resulted in 32% decolorization. Dotto et al.,¹⁵ studied that maximum adsorption of methylene blue takes place by ultrasonic surface-

modified chitin (26.7mg/g) within 6 hours. Zhou¹⁷ and his colleagues did experiments to remove MB using cellulose-graft acrylic acid hydrogels and stated a capacity of 2197mg/g equilibrium adsorption in 33.3 hours. Zeng et al.,¹⁸ revealed that magnetic uptake of methylene blue dye by chitosan (24.7mg/g). He et al.,¹⁹ studied the methylene blue adsorption using nano crystalline cellulose with a maximum adsorption capacity of 101 mg/g reported in ten minutes. Fan²⁰ and his colleagues explained an adsorption capacity of cyclodextrin-chitosan (CDC) - Fe₃O₄ nano composite (2.78g/g) methylene blue removal in 50 minutes. Fabbicino & Pontoni¹¹ explains adsorption of chitin-containing residues and the removal percentage was obtained up to 90% using 2.1mg/ml of dried raw shells for the tested dyes in 2 hours. Cao²¹ and his colleagues depicted 79.8% of methylene blue adsorption using 3.5% lower crystallinity and porous chitin. The study carried by Dhanasekaran⁸ and co-workers the adsorption percentage increases with increase in concentration of chitin nano particle from 15 to 95% within 30 minutes at a constant initial MB dye concentration (10mg L⁻¹) in 15mL solution and a higher adsorption was seen in 6mg L⁻¹.

Conclusion

Holistic approach to environmental management of industrial waste using shrimp shell extract is outlined. The usage of shrimp shells as bio-adsorbents give two way benefits by solving environmental solid waste disposal issues and economically by reducing the cost of water treatment. Different parameters like adsorbent amount and contact time were monitored and the optimum dye reduction (93.23%) was obtained at an adsorbent amount of 4 gram at a contact time of 4 hours.

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Conflicts of interest

The authors have no conflict of interest.

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