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Removal of Methylene Blue by Adsorption Using Fish Scale Chitin

Merina Paul Das†, Renuka M., Vijaylakshmi J. V., Suguna P. R. and Karpuramprasad
Department of Industrial Biotechnology, BIHER, Chennai, India
†Corresponding author: Merina Paul Das

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ABSTRACT

In the present study, chitin was extracted from fish scale waste and utilized as an adsorbent to remove the toxic dye, methylene blue from aqueous solution by a batch adsorption process. The abundant source of fish scales direct the production of chitin, as a low-cost adsorbent. Dye adsorption studies were carried out to determine the effects of contact time, pH, initial concentration of adsorbate and adsorbent dosage on dye removal. The characterization of the adsorbent was done by scanning electron microscope (SEM), X-ray diffractometer (XRD), and fourier transform infrared (FTIR) spectrophotometer. The micrograph revealed the porous structure of chitin, while XRD and FTIR confirm the crystalline and structural information of the chitin, respectively. The results of dye adsorption study revealed that the removal efficiency of dye using chitin was significant at pH 8 after 90 min of dye-adsorbent contact time. The optimum amount of adsorbent was found to be 2g/L. Hence, chitin can be used as cheap, efficient, ecofriendly adsorbent for the removal of dye from effluents.

INTRODUCTION

A large number of dyes are commonly used in leather, textiles, cosmetics, paper, printing and food-processing industries. These are synthetic organic dyes such as nitro, azo, indigo, etc. that are lost in wastewater during formulation and processing (Neamtu et al. 2002). It is estimated that azo dyes are most extensively manufactured and used dyes among all, approximately 60% of the total dyes (Ayed et al. 2011). The toxic dyes discharged from the industries affect directly the water sources by colouring, and indirectly damage aquatic environment by blocking sunlight, inhibiting aquatic photosynthesis and re-oxygenation ability of water bodies, thus causing a great disorder in the natural growth activity of living organisms and food-web (Guyer & Lnce 2003). Conventional water treatment process cannot degrade the synthetic dyes because of their complex aromatic ring structure, recalcitrant nature, hydrophilic property, and resistant to light, heat, chemicals, causing sustainable hazard in human health and environment (Li et al. 2012, Ghosh et al. 2015). Toxicity and mass production of dyes, therefore, leads to the necessity of treatment of such dye-containing wastewater. Among the organic dyes, methylene blue (MB) is one of the colour pollutants which cause undesirable effects on environment (Chen et al. 2010). MB (3,7-bis (dimethylamino)-phenothiazin-5-ium chloride) is a cationic dye, widely is used for dyeing fabrics, colouring paper, etc. It was found that even at low and moderate doses, MB increase the arterial blood pressure, whereas at higher dose, it causes systemic hypotension, vomiting, heinz body formation, mycocardardial depression, cyanosis, shock and tissue necrosis in humans (Mohabansi et al. 2011).

Traditional methods like coagulation, precipitation, filtration, sedimentation, flocculation, electrodialysis, neutralization and oxidation were used in order to remove the azo dyes from the dye wastewater before disposal (Kumar et al. 2012). These physico-chemical methods are not economically feasible because they can transform the dyes from one phase to another leaving the problem essentially unsolved. Adsorption is a physico-chemical method of wastewater in which the dissolved material is attached to an adsorbent surface by means of different interactions like Van der Waals force, electrostatic interaction, depending on the adsorbent and the dye composition (Ebrahimi et al. 2013). Passive uptake or adsorption of dyes on a dead or inactive bio-based material is one of the most promising alternatives for dye removal from wastewater. The biomaterial as adsorbent has many advantages over the other methods including, higher efficiency, high selectivity at molecular level, cost-effective, easy operation, low energy consumption, and reusable (Shah et al. 2013).

Chitin, is an insoluble linear (β-1,4-linked homopolymer of N- acetylglucosamine) and natural renewable biopolymer. It is most abundantly found in exoskeleton of fungi, marine animals and insects (Das et al. 2012). Chitin has better adsorption capacity and can be used for desorption of a wide range of substrates, such as dyes, heavy metals and other pollutants easily, due to the presence of amino group in its structure (Khedr et al. 2012).

Fish scales are rich source of chitin and daily abundant scales are discarded from the fish processing industry, fish market, etc. This huge waste may cause environmental hazard. Thus, the use of this waste to produce biologically renewable material such as biopolymers is a challenge in recent scientific research and development (Muslim et al. 2013). In this regard, chitin was extracted from fish scale waste and its adsorption efficiency was investigated against methylene blue.

MATERIALS AND METHODS

Materials

The azo dye, methylene blue [3, 9-bis dimethyl-aminophenazo thionium chloride] was procured from Sigma -Aldrich, Mumbai. Hydrochloric acid (HCl), and sodium hydroxide (NaOH) pellets were purchased from Hi-Media, Mumbai. All the reagents used in this work were of analytical grade. Distilled water used throughout the reaction studies.

Collection and Pretreatment of Materials

Fish scales of *Labeo rohita* with an average body weight of 100-200 g were collected from the coastal areas of Guntur, India. The scales were removed from the skin, kept in iced plastic bags and transported to the laboratory. The scales were washed with tap water followed by twice with distilled water to clean and dried at room temperature. Finally, the scales were ground into small pieces and kept at 4°C until further use.

Extraction of Chitin

To remove calcium carbonate from the scales and prevent the chitin hydrolysis, the scales were soaked in 1N HCl for 24 h with constant stirring at 30°C. The fish scales, then were washed with distilled water for several times until neutral pH reach. For deproteinization, the fish scales were dipped into 0.5% of NaOH (1:1 m/v) and incubated for 30 min at 95°C in an oven. Again they were washed with distilled water until becoming neutral. Finally, the scales were dried at 80°C in hot air oven for 4 h. The fish scales were made as fine chitin powder and kept in air tight container for experiments (Puvvada et al. 2012).

Characterization of Chitin

Morphological characterization: Scanning electron microscopic (FEI Quanta 200 SEM) technique was adopted to observe the microstructure of chitin powder. The surface of chitin was coated with gold in vacuum using sputter coater, and was photographed.

Powder XRD studies: The relevant phases of chitin powder were determined by X-ray diffractometer (XRD) (X'Pert Pro A Analytical) operated at 45 kV voltage and 40 mA current. The XRD profile was recorded by Cu kα radiation source in a θ-2θ configuration.

FTIR analysis: To determine the functional groups on the chitin powder surface, fourier transformed infrared spectroscopy (FTIR) analysis was carried out on the crystal cell of the FTIR spectrophotometer. The FTIR spectra were recorded at resolution of 4 cm^{-1} in the transmission mode (4000-400cm^{-1}) using a FTIR spectrophotometer (Jasco-FTIR 4100type A, Japan).

Batch adsorption experiments: For decolorization studies, a stock solution of methylene blue (1000 mg/L) was prepared with distilled water. In each adsorption reaction, an accurately weighed amount of chitin powder was added to the aqueous methylene blue solution and the mixture was stirred at 250 rpm for respective incubation time at 27°C. After incubation, adsorbent was separated from solution by centrifugation and residual dye concentration in the supernatant was determined by measuring the absorbance at 668 nm using UV-vis spectrophotometer (UV 8500 II Techomb). The effect of different parameters such as initial dye concentration (10-60 mg/L), time (30-180 min), chitin dosage (0.5-3 g/L), pH (3-10) on the adsorption of chitin was carried out. Removal of dye was expressed in percentage and calculated as (Das et al. 2016):

$$\%\ \text{Dye removal} = \frac{\text{Initial absorbance-Final absorbance}}{\text{Initial absorbance}} \times 100$$

RESULTS AND DISCUSSION

Isolation and Characterization of Adsorbent

After demineralization by acidic treatment and deproteinization by alkali treatment of fish scales of *L. rohita*, the scales were dried to get chitin in powder form. The size of the obtained biopolymer was reduced to get maximum surface area to volume ratio. The greater surface area leads to the formation of larger number of active sites to adsorb more amounts of adsorbate molecules.

Morphological characterization of chitin extracted from fish scale waste was carried out using SEM. The micrograph represented in Fig. 1 clearly shows that wide variety of pores are present in the obtained biopolymer along with some fibrous structure. There are some holes also found on the surface of the chitin, which would have used for active site for adsorption process.

To confirm the structure of extracted biopolymer, an XRD pattern (Fig. 2) was recorded in the 2θ range from 5-40°. The powder XRD of chitin shows strong diffraction peaks at 2θ value of 9.6°, 19.1°, 20.1° corresponding to the (0 2 0), (1 1 0), (1 2 0) and (1 3 0) sets of lattice planes

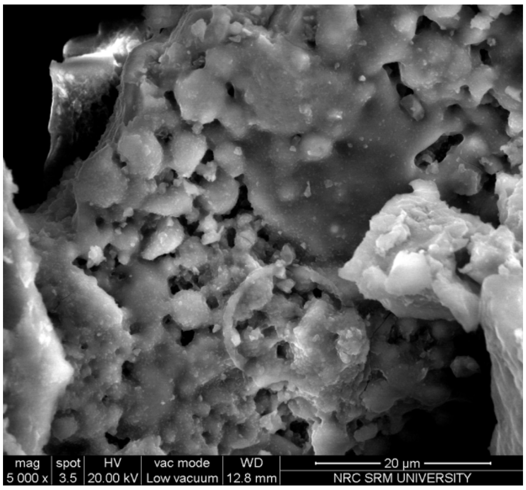

Fig. 1: SEM image of chitin.

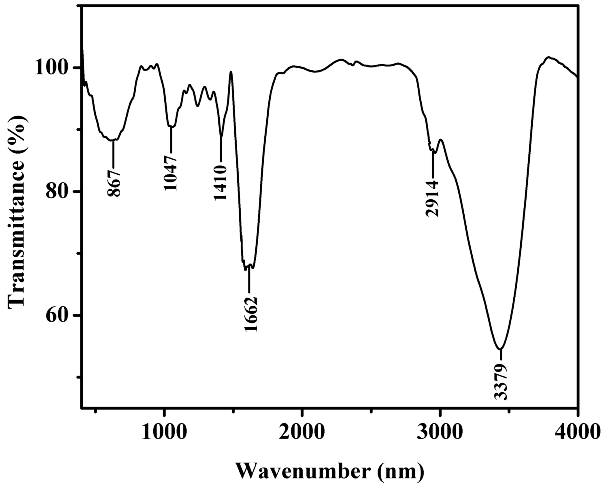

Fig. 3: FTIR absorption spectrum of chitin biopolymer.

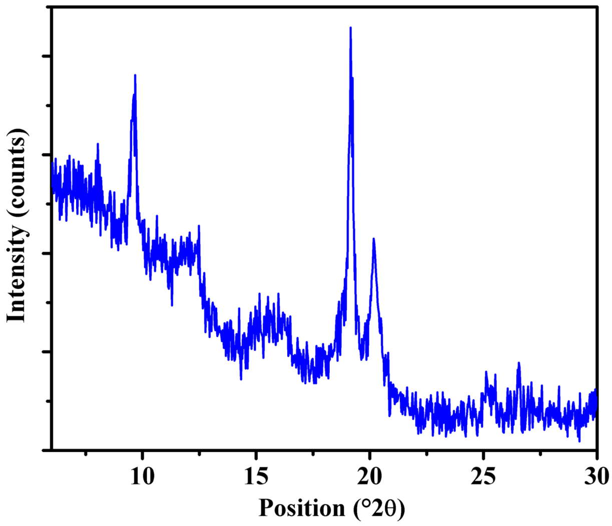

Fig. 2: X-ray diffraction pattern of chitin.

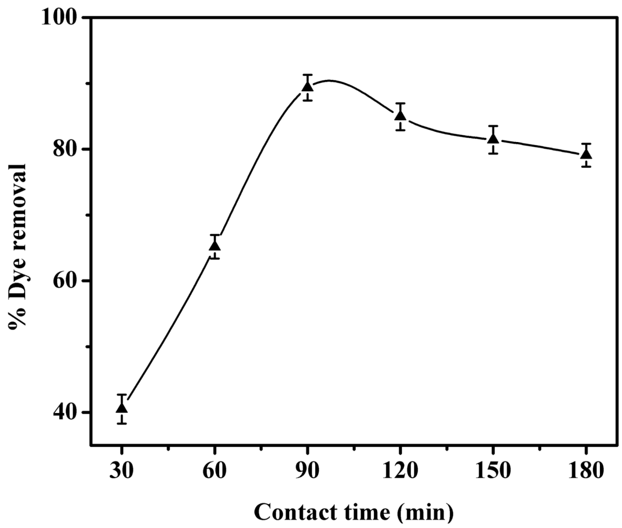

Fig. 4: Effect of contact time on the adsorption of MB.

(JCPDS file no. 351974). The intense broad peak at 2θ value of 19.1° depicts the smaller size of the chitin particle and reflects the growth of the crystal nuclei (Becheri et al. 2008). Thus, XRD pattern proves that the positions of these peaks indicate the crystalline nature of the chitin.

FTIR spectroscopic analysis of chitin was represented in Fig. 3. The spectrum shared the strong IR peak positioned at 3379 cm^{-1} arise from stretching vibration frequencies of aliphatic O-H bond, the band at 2914 cm^{-1} is assigned due to sp^3 C-H stretching mode (asymmetric and symmetric) from acetamide ($-NHCOCH_3$) group. The presence of absorption band at 1662 corresponds to amide I (C-N of ($NHCOCH_3$) and stretching vibration of C=O), whereas the band at 1410 cm^{-1} was assigned due to CH_2 bending and CH_3 deformation. Absorption spectra arise at around 1047 cm^{-1} can be attributed to -C-O-C- bond of glucosamine ring, and the peak at 867 cm^{-1} is responsible for characteristic CH deformation of the β-1, 4 glycosidic bonds of N-acetyl-D-glucosamine of chitin (Das et al. 2017a, Das et al. 2017b, Zaku et al. 2011). It is clearly observed from the infractrogram that the spectrum is similar to the most significant parts of pure chitin, indicating the good quality of chitin extracted from fish scales. The spectrum showed a series of sharp adsorption bands due to the crystal nature of the chitin, hence supports the results of XRD.

Dye Adsorption Studies

Effect of dye-adsorbent contact time on efficiency of dye removal: The influence of different contact times (30-180 min) for adsorption of MB on chitin with constant pH (7),

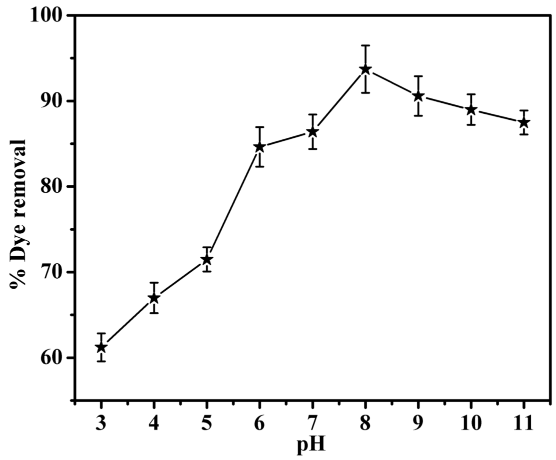

Fig. 5: Effect of pH on the removal of dye by using chitin.

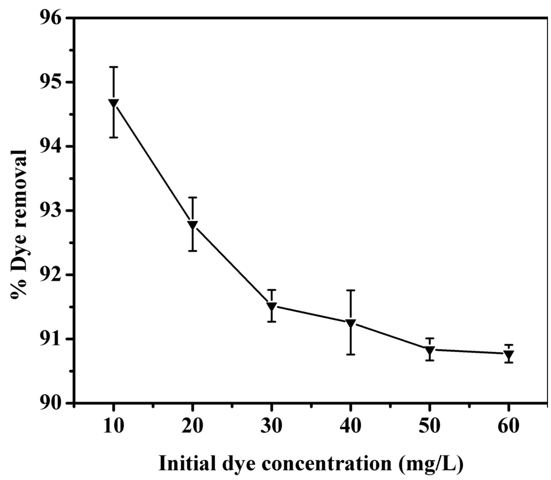

Fig. 6: Effects of initial dye concentration on dye adsorption.

adsorbent dose (1 g/L), dye concentration (30 mg/L) was depicted in Fig. 4. At the beginning, the rate of dye removal percentage increased with increase of contact time until it reaches to equilibrium. Further, with the increasing of adsorption time the adsorption rate gradually decreases. The optimum contact time was found to be 90 min to remove 89% of the dye from the aqueous solution. At the initial stages of adsorption reaction, the dye adsorption was very fast due to the availability of the adsorption site on chitin surface. But after the equilibrium, there was no significant change found in dye removal due to the saturation of adsorption site, percentage dye removal was almost constant at higher contact time with same amount of adsorbent dose (Rodriguez & Mazzoco 2010, Rahman et al. 2016).

Effect of pH on methylene blue adsorption on chitin: pH of the medium provides a critical role in adsorption of dye from the solution because it affects the solubilization of dye and concentration of ions present on the adsorbent surface. To study the effect of pH on percentage of dye removal, the reactions were carried out at different pH ranges from 3-11 with 30 mg/L of initial dye concentration and 1 g/L of the adsorbent dose for 60 min. As seen from Fig. 5, the dye adsorption efficiency of the chitin increases with increase in pH and reaches the optimum value of 92% at pH 8. MB belongs to cationic dye and form positive charge in aqueous solution. Chitin is also a positively charged biomolecule. At the acidic pH, the high concentration of proton (H^+ ions) in solution compete with MB cations for the vacant adsorption sites of positively charged chitin causing decrease in dye adsorption. But at the higher pH, the chitin becomes negatively charged and favours the adsorption of cationic MB dye due to increased electrostatic interactions (Srinivasan et al. 2013, Dermibas et al. 2008).

Effect of initial concentration of dye on adsorption: In order to determine the effect of initial dye concentration on batch adsorption, a varied range (10-60 mg/L) of MB concentration was tested at pH 7 on 1 g/L of chitin for 60 min. Fig. 6 shows that increase in initial MB concentration leads to increase in percentage of dye removal by chitin. The initial dye concentration plays an important role to control the mass-transfer resistance of the dye, because the presence of concentration gradient of dye in liquid (aqueous solution) and solid (adsorbent) phases is the driving force for the adsorption process (Idris et al. 2011). At higher initial dye concentration, the increase in concentration gradient between MB and chitin results in increase in the adsorption capacity.

Effect of adsorbent dose on dye adsorption on chitin: Fig. 7 represents the effect of amount of chitin powder on percentage of dye removal from aqueous MB solution. The study was carried out with varying dosage of adsorbent from 0.5 to 3 g/L with constant initial dye concentration of 30 mg/L and at pH 7. The optimum dye removal was 95% attained for adsorbent dose of 2.0 g after 60 min of incubation. Further, with increased chitin dosage, the percentage of dye adsorption decreased due to improper dye-adsorbent interaction. At the beginning, adsorption efficiency was low because the adsorption site on the adsorbent surface could not effectively contact with the dye. When the adsorbent amount increased, the adsorbent dose provides a larger number of active sites on the greater surface area, thus increasing percentage of dye removal. Above the optimum amount, the removal percentage decreased with increase in adsorbent dose because all adsorption sites of adsorbent were occupied by the adsorbate molecules and no sites available for further dye adsorption (Shirsath & Shrivastava 2012, Bello & Ahmad 2011).

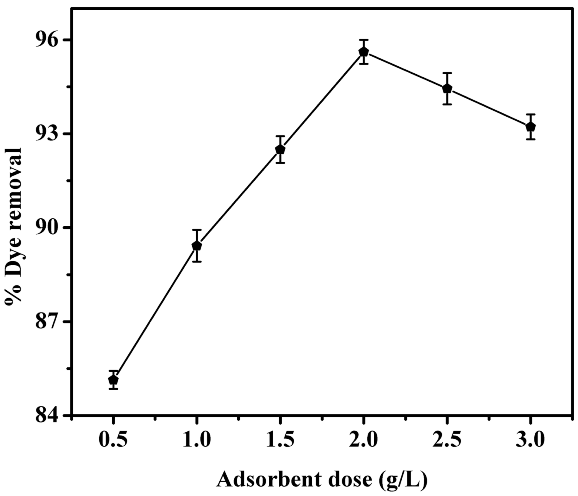

Fig. 7: Effects of adsorbent on the removal of methylene blue.

CONCLUSIONS

Development of suitable material to control the rapidly growing aqueous toxicity is an increasing demand in current scenario of industrialization. Chitin, successfully extracted from the fish scale waste, provides a renewable material that can be used for treatment of effluent. The obtained polymer was characterized to verify its morphological and structural properties. SEM, XRD and FTIR confirm the functional properties of the chitin. The result of the dye adsorption by using chitin reveals that this natural biopolymer can be used commercially for dye remediation. This simple, inexpensive and effective approach may be employed to successfully minimize the colorant pollutants from the effluent.

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