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Biodecolourisation of Textile Dye Effluent Using Chitosan

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Abstract: *The major problem in textile industries is the effluent treatment particularly the removal of dyes. Polymer adsorbents are widely tried in the removal of dyes from industrial effluents. Chitosan, a biopolymer derived from chitin is most abundantly present in the exoskeleton of crustaceans including prawns, shrimps, lobsters and crabs. In the present study, efficiency of chitosan as a biosorbent in the treatment of textile dye effluent has been analyzed. It has been found that chitosan is very effective in biodecolourisation of textile dye effluent collected from the local dyeing units. It has also reduced the physico-chemical parameters to the permissible limits. The results have been confirmed using HPLC and statistical analysis. From the present study it is found that chitosan isolated from the chitin of prawn shell waste is very effective in terms of biodecolourisation of textile dye effluent as well as cost.*

Keywords: *Biodecolourisation, Textile Dye Effluent, Chitosan, Biosorption, Dyes.*

INTRODUCTION

Deterioration of environmental quality has become the major problem of the modern world. Industries are the major contributors of air, water and land pollution, leading to loss of health and life throughout the world. Organic and inorganic contaminants such as suspended solids, dyes, pesticides, toxicants and heavy metals are heavily present in industrial effluents which are released in to the water bodies without proper treatment. This creates a serious problem in the environment and also affects the water quality when discharged into fresh water sources. Hence the contaminants must be effectively removed to meet prescribed standards (Robinson et al., 2001).

The Textile industry is an aggregation of several industrial units which use both natural and synthetic fibres to produce textiles. In such textile industries, synthetic dyes are mostly employed. At the end of the textile processing, significant level of dyes particularly synthetic dyes enters into the environment in the form of waste water (Olukanni et al., 2006). Effluents discharged from textile and dyeing units have to be treated due to their effect on aquatic ecosystems and their toxicity and carcinogenicity. The complex structures of different dyes make dye effluent treatment difficult by conventional biological, physical and chemical methods. Therefore, innovative treatment technologies need to be analyzed (Slokar and Marechal, 1998).

The biosorption of dyes by natural biopolymers has been widely studied for industrial applications because of their ability to reduce metal concentrations. It is well-known that chitosan, the nontoxic and biodegradable polymer can be used effectively in wastewater treatment. Enormous amount of waste is generated at the end of prawn processing industries and that could be used effectively as a raw material for the production of chitosan (Stevens, 2001). Hence the present study has been designed to test the potential of chitosan in the decolourisation of textile dye effluent.

Materials and Methods

Sample collection

The textile dye effluent was collected from a textile dyeing unit at Avaniapuram, Madurai, Tamil Nadu, India. The sample was analysed for the various physico-chemical parameters such as total dissolved solids (TDS), electrical conductivity, pH, total hardness (TH), total alkalinity, calcium, magnesium, nitrates, chlorides and phosphates.

Isolation of Chitosan

The shell wastes of prawn species namely, *Penaeus indicus* and *Metapenaeus affinis* were collected from a fish stall at K.Pudur, Madurai. The shells were processed, washed and sun dried. Dried shells were ground in a mixer grinder. Ground shells were subjected to 1.5 N HCl treatment for two hours. This step is for demineralization. Demineralized shells were washed to remove the traces of acid. Then the shells were boiled in 3% sodium hydroxide for 30 minutes to remove the proteins present in the shells. This yields chitin. After deproteinization, the shells were washed and subjected to deacetylation by heating in 1.1% sodium hydroxide at 95-100 ˚C for 90 minutes. The resulting product was washed to obtain pure chitosan.

Preparation of test solution

10, 20, 30 and 40% of dye effluent concentrations were prepared for both 100ml and 1000ml.

Decolourisation study

20g of isolated chitosan was introduced into the textile dye effluentconcentrations. Initial absorbance was measured and the solution was observed periodically.

Estimation of absorbance

The samples were taken in a cuvette and placed in the colorimeter. The absorbance was noted periodically at a time interval of 48 hours at the wave length of 570 nm.

Decolourisation assay

The decolourisation activity was expressed in terms of percentage decolourization as determined by monitoring the decrease in the absorbance at 570 nm. Decolourisation activity was calculated according to the formula:

$$\text{Decolourisation activity (\%)} = \frac{(\text{Initial absorbance}) - (\text{Observed absorbance})}{\text{Initial absorbance}} \times 100$$

HPLC analysis

The sample containing 10% concentration of textile dye effluent was subjected to HPLC analysis before and after treatment.

Statistical analysis

Two way analysis of variance (ANOVA) was done for the dye effluent with the variables, treatment period and dye effluent concentration applying Microsoft excel package.

Results and Discussion

The textile industry and its products result in several environmental and toxicological impacts. In textile industries, more amounts of chemicals are required to produce finished fabrics which are the real root cause for the environmental problems. Synthetic dyes are employed in industries like textiles, leather, paper and plastics for coloring (Chiou and Li, 2002). Reactive dyes are commonly used due to their advantages (Uzun, 2006). Dyes are a very important source of metals in finished textiles. Typically transition metals such as chromium, copper, nickel and cobalt are used (Rybicki, 2004). It is difficult to remove dyes from waste waters because they are highly stable. These dyes cannot be easily degraded (Mittal, 1996).

In recent years, adsorption becomes the most popular technique in waste water treatment due to its competency in the removal of pollutants too stable for biological methods. This can produce high quality water while also being a process that is economically feasible. Adsorption technique has several advantages (Chern and Huang, 1998). Adsorption is an efficient method to remove pollutants from wastewater. Also, the adsorption bestows a fascinating substitute treatment, particularly if the sorbent is of low cost and most commonly available (Nomanbhay and Palanisamy, 2005). Cheap adsorbents are very important in developing countries like India (Ravikumar et al., 2007). The use of cheap waste materials in the treatment process of wastewaters containing dyes has received attention recently.

Chitosan is a biodegradable biopolymer and abundant in nature. It has been tried in industrial waste water treatment. In the present study, the chitosan isolated from prawn shell wastes was tested for its adsorption capacity in treating textile dye effluent. The collected textile dye effluent exhibited certain parameters that exceed the maximum permissible limits. These physico-chemical parameters showed drastic reduction after treatment with chitosan as shown in Table 1. Hassan et al. (2009) also noticed similar kind of results in their studies on chitosan for textile waste water treatment. The textile effluent showed maximum absorbance at 570 nm. The absorbance was recorded in the various experimental concentrations regularly. The changes in the absorbance values after decolourisation are shown in Fig.1. There was a steady decline in the absorbance as the treatment period increased. This may be due to the saturation of active sites (Hadi, 2013).

Decolourisation can be through adsorption and ion exchange. Dye concentration, dose of the adsorbent and contact time, are the important parameters in adsorption studies. The adsorbent dose decides the efficiency of the adsorbent for a particular dye concentration during specific contact period (Crini et al., 2007). In the present study, removal of dye in 10, 20, 30 and 40% in textile effluent concentrations by chitosan was studied during different contact time periods (0, 2, 4, 6, 8 and 10 days). The dye removal activity of chitosan varied depending upon the initial concentration and contact time (Fig.2). It was evident that the quantity of dye adsorption by chitosan decreased with the increase in textile dye effluent concentration. Chitosan was found to decolourise effectively in the lowest effluent concentration (10% of dye effluent). Natarajan et al. (2011) reported that, at lower concentration, the ratio of dye to surface area is low and adsorption is independent of initial concentration. The adsorption sites available are very less at high concentration. So, the percentage of dye removal is always based on concentration. Figure 2 also shows increase in removal efficiency with increase in treatment period. More time is available for the dye to be in contact with chitosan. So, dye removal is increased steadily over the treatment period of experiment. It is concluded that textile dye has to be treated with chitosan for ten days to achieve maximum removal percentage.

High performance liquid chromatography (HPLC) is a powerful analytical technique to confirm biodegradation. The appearance of new peaks at different retention times along with disappearance of major peaks when compared with the original dye is an indicator of biodegradation and formation of some new compounds (Fisher et al., 1990). In the present study, HPLC analysis of the untreated 10% textile dye effluent showed numerous peaks but after treatment with chitosan, these peaks were replaced by new peaks. The results of HPLC analysis clearly indicated the degradation of textile dye effluent by chitosan. After incubation under static conditions, the disappearance of major peaks and appearance of new peaks in the chitosan treated sample was observed when compared to untreated sample. It is thus rational to propose that these peaks represent degradation of the effluent. The HPLC profile of the untreated sample showed major peaks at 2.437, 2.560, 2.840, 3.800, 4.643, 5.243, 6.230 and 6.450 min (Fig.3a), while the chitosan treated sample showed peaks having different retention times 2.800, 2.953, 3.990, 4.790 and 5.437 min (Fig.3b) than that of the untreated sample. Absence of peaks in treated sample corresponding to that of the untreated sample indicated complete biotransformation of the effluent to other simpler products and confirmed biodegradation of the effluent by chitosan. This again supports the degradation and also ensures the safer disposal of chitosan treated textile effluent into environment (Khandare et al., 2014). The two way analysis of variance for the variables namely, textile dye effluent concentration and treatment period showed statistically significant variation in biodecolourisation. The variation due to the treatment period was statistically significant for the effluent treated with chitosan (Table 2).

In recent days, use of natural and effective sorbents has so much attention in the expansion of waste water treatment technologies. Of biosorbents, chitin is characterized by a high adsorption capacity (Filipkowska et al., 2002). Chitosan with higher amino group content was reported to be more effective for binding dyes than chitin. Chitin and chitosan are adsorbents which contain amine or amide nitrogen in varying proportions (Safarik, 1995). These groups can offer a higher capacity of adsorption towards acid dyes or anionic dyes. Adsorption can occur by Van der Waal's attraction, hydrogen bonding and coulombic attraction. Adsorption and ion exchange are responsible for decolourization. Factors like, interaction between dye and sorbent, surface area of the sorbent, size of the particle, temperature, pH and treatment time also influence decolourisation. It was found that the efficiency of decolourisation increases as the period of treatment increases (Kyzas et al., 2013).

Conclusion

Chitosan is a biowaste material which is easily available at a low cost and also used as a successful adsorbent for the removal of dyes in the effluent. The optimization study has been investigated under different experimental conditions for the biodecolourisation of textile dye effluent using chitosan. Chitosan was found to decolourise effectively in the lowest concentration of effluent. HPLC analysis of the textile dye effluent showed that there were variations in the retention times of the peaks between the experimental and control samples. From the above study it is clear that chitosan is efficient in the biodecolourisation of the textile dye effluent.

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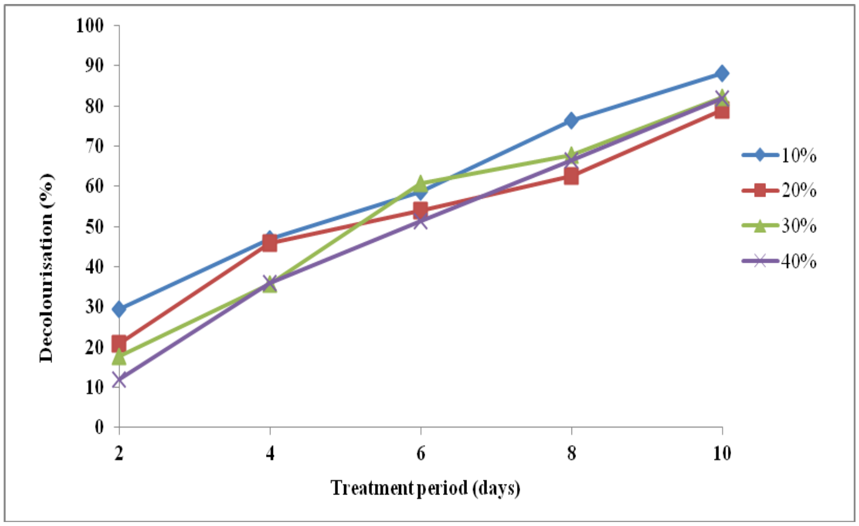


Figure 1. Effect of chitosan treatment on the decolourisation of textile dye effluent

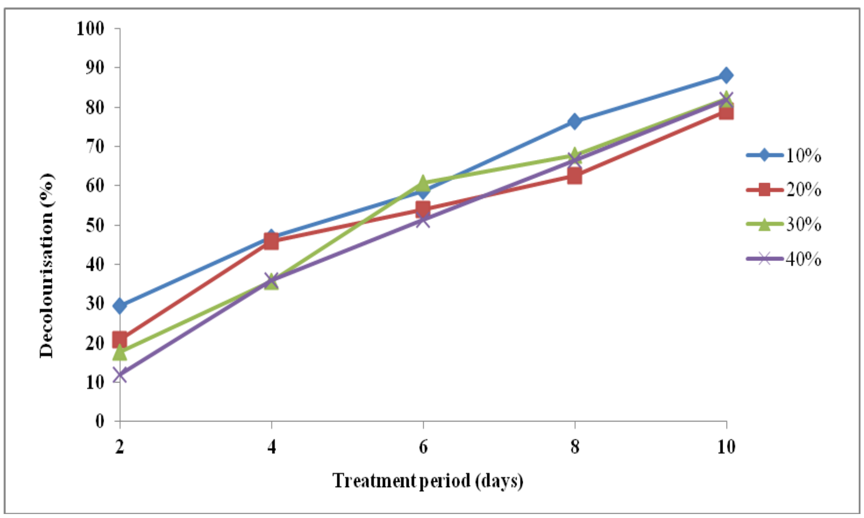
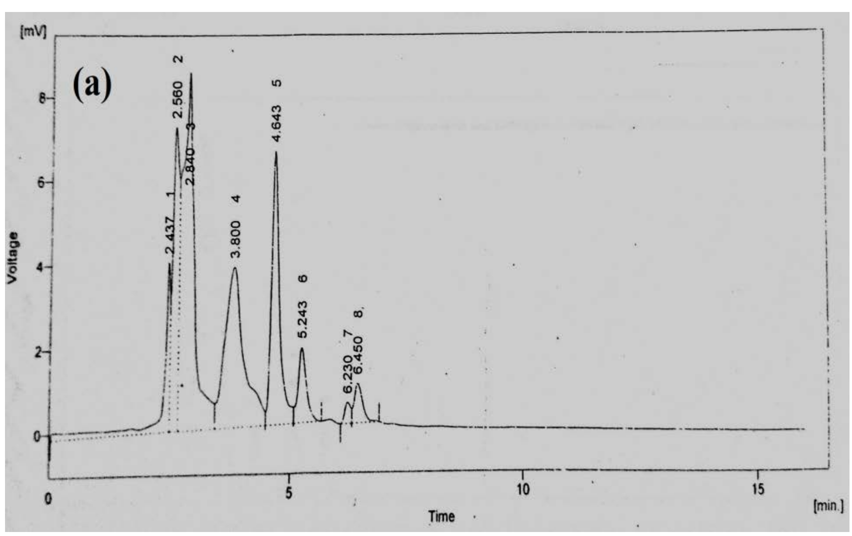


Figure 2. Decolourisation activity of chitosan on textile dye effluent



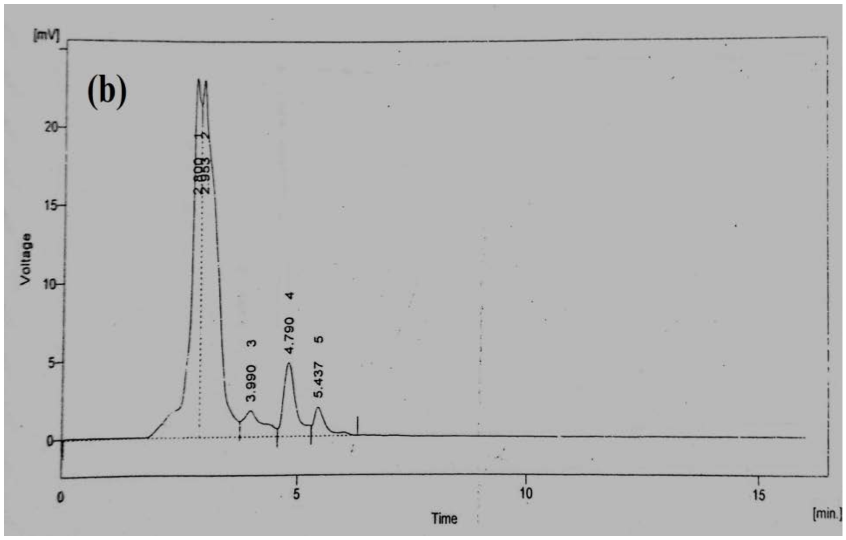


Figure 3. HPLC analysis of 10% textile dye effluent: (a) untreated (b) treated using chitosan

Table 1. Physico - chemical properties of textile dye effluent before and after treatment with chitosan

S.No	Parameters	Permissible limits (as per TNPCB*)	Untreated effluent	Chitosan treated effluent
1.	Total Dissolved Solids (mg/l)	5000 - 2000	3150	400
2.	pH	7.0 – 8.5	7.43	6.88
3.	Total Hardness (mg/l)	200 – 600	1000	220
4.	Total alkalinity (mg/l)	200 – 600	660	150
5.	Calcium (mg/l)	75 - 200	120	48
6.	Magnesium (mg/l)	30 - 150	168	24
7.	Iron (mg/l)	0.1 – 1.0	0.19	0.13
8.	Manganese (mg/l)	0.05 – 0.5	0	Nil
9.	Nitrates (mg/l)	45 – 100	21	4
10.	Chlorides (mg/l)	200 – 1000	1200	460
11.	Phosphates (mg/l)	Nil	0.26	0.16

* TNPCB – Tamil Nadu Pollution Control Board

Table 2. ANOVA for the decolourisation of textile dye effluent using chitosan

Source of Variation	SS	dF	MS	Calculated F Value	F table Value at 5 % level	Level of Significance
Concentration	292.3695	3	97.4656	6.579231	3.4903	Significant
Treatment period	9444.607	4	2361.15	159.4	3.25916	Significant
Error	177.753	12	14.8128			
Total	9914.729	19				