

Research Article

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# Textile Dye Removal from Wastewater Effluents Using Chitosan-ZnO Nanocomposite

Arafat A\*, Sabrin A Samad, Dilruba Huq, Mohammad Moniruzzaman and Shah Md. Masum Dhaka University, Bangladesh

#### Abstract

Textile dyeing industry effluents require advanced treatment technologies such as adsorption for the removal of dyestuffs. In this Study Chitosan Zinc Oxide Nano composite was used as an adsorbent for removal of sample that contains two reactive dyes: Reactive Black HN and Reactive Magenta HB from textile dying industry effluent. The color removal performance of Chitosan Zinc oxide Nanocomposite has been investigated using parameters such as temperature, composite loading, time of contact and turbidity. It was found that composite exhibits dye removal efficiency that is about 95-99%. Batch adsorption studies of color removal from effluents of Textile dyeing industry were carried out using Chitosan-zinc oxide Nano particles composite. Results showed that color adsorption increases with the increase of the dosage of composite. In this study, optimum dosage was found for the removal of dye from Textile effluents. It was found that using 2 gm of Composite per liter of effluent at ambient temperature (50°C) and 60 minutes time of contact, it may be possible to remove 99% of the original color of the effluent.

**Keywords:** Adsorption; Chitosan-ZnO Nano composite; Textile effluent; Removal efficiency

#### Introduction

Effluent from textile industry is a major source of environmental pollution especially water pollution. Among the various stages of textile industry, dyeing plant is the most pollutant stage. The textile dyeing wastes contain unused or partially used organic compounds, strong color and high COD and BOD. The intensity of pollution depends on the fabric, as well as dyes and chemicals used in textile industries, their fixation rate on the fabric. Beside that the dyeing sequence, dyeing equipment and the liquor ratio used in the textile industries can also affect the pollution intensity. Colored organic effluent is produced in industries such as textiles, rubber, paper, plastic, cosmetics, etc. Discharging of dyes into water resources even in a small amount can affect the aquatic life (Figure 1). Therefore, colored wastewater cannot be discharged without adequate treatment. As dyes are designed to resist breakdown with time and exposure to sunlight, water, soap, and oxidizing agent, they cannot be easily removed by conventional wastewater treatment processes due to their complex structure and synthetic origins. Thus, dye removal has been an important but challenging area of wastewater treatment. To remove dyes and other colored contaminants from wastewaters, several physical, chemical, physico-chemical and biological methods have been developed. Among these methods, adsorption has been found to be one of the most popular physico-chemical treatment methods for removing dyes with potential applications [1]. It has been reported that many different types of adsorbents are effective in removing color from aqueous effluent. Natural polymeric materials are gaining interest for application as adsorbents in wastewater treatment due to their biodegradable and non-toxic nature [2]. Chitosan (CTS) is the N-deacetylated derivative of chitin and the second most plentiful natural biopolymer. As a wellknown sorbent (Figure 2), CTS is widely used for the removal of heavy, transition metals and dyes [3,4]. Nevertheless, the market cost of CTS is relatively high and its specific gravity should be improved for practical operation. Therefore, several attempts have been made to develop cheaper and effective adsorbents.

Dyes are recognized as micro-toxicants and their acute and short-term effects have long been recognized. The complex organic framework of dyes and presence of heavy metals induce chronic



toxicity and they may be mutagenic, teratogenic and carcinogenic. Many investigators reported several cases of tumors, cancer and effect on liver and kidney after long term exposure (Figure 3). The most obvious impact of the discharge of dye colored effluent is the persisting nature of the color, which is stable and fast, difficult to degrade, toxic and inhibitory, and render the receiving water unfit for its intended use [5]. Various physical, chemical, physico-chemical and bio-chemical processes like sedimentation, equalization, neutralization, flotation, chemical oxidation/reduction, chemical precipitation, coagulation and

\*Corresponding author: Arafat Abul, Dhaka University, Bangladesh, E-mail: anikarafat11@yahoo.com

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flocculation, adsorption, ion exchange, reverse osmosis, electrochemical coagulation, etc. have been investigated for treatment of dye effluents [6-12]. Among all these processes, the adsorptive process is a sludge free process, and using as a sorbent is found to be effective in removal of dye color and is firmly established as most reliable one [13].

Adsorption method is a prominent method of treating aqueous effluent in industrial processes for a variety of separation and purification purpose. This technique also was found to be highly efficient for the removal of color in terms of initial cost, simplicity of design, ease of operation and in sensivity to toxic substances. Adsorption is undoubtedly the most important of the physicochemical processes responsible for uptake of inorganic and organic substance in the aqueous environment. Factors such as pH, nature and concentration of substrate and adsorbing ion, ionic strength, and the presence of competing and complex ion affect the extent of adsorption. Chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity and adsorption properties (Figure 4). Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve the active sites. Recently, hybrid materials based on chitosan have been developed, including conducting polymers, metal nano particles and oxide agents, due to its excellent properties of individual components and outstanding synergistic effects simultaneously.

Novel bio composites, commonly known as Hybrid composite considering their particle size, such as Chitosan-Zinc Oxide Nano particles, have the potential to act as alternative low-cost adsorbents. This nanocomposite frequently exhibit remarkably improved mechanical





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and materials properties and are attracting considerable interest in polymer science field. The main mechanism of dye adsorption was found to be a spontaneous charge associated interaction.

There are some characterization technique such as threedimensional optical microscope, electrochemical work station, scanning electron microscope equipped with electron backscatter diffraction, X-ray Diffraction, Fourier Transform Infrared Spectroscopy and Thermogravimetry analyzer [11]. Results showed that the surface modification brings in surface strengthening effect and improved surface corrosion resistance performance. It is indicated that refined surface layer were obtained on account of dynamic recrystallization (DRX) and phase change, which was implemented at low temperature and high strain rate [9].

Thus, in this study, it is aimed to prepare hybrid chitosan and zinc oxide Nano particles and to study its ability as an adsorbent for removal of color from textile effluent. The effects of adsorbent dosage, settling time, initial dye concentration and temperature on the performance of hybridized adsorbent towards removal of color in wastewater were also been investigated in this study.

#### Materials and Method

#### Sample collection

The sample effluents was collected from ABC Knit dyeing and finishing mills Ltd. situated in Kadamtali, Shyampur, DHAKA. The sample contains two reactive dyes: Reactive Black HN and Reactive Magenta HB. The adsorbents used for this study is Chitosan ZnO Nanocomposite. Chitosan ZnO Nanocomposite was prepared from Chitosan and ZnO nanoparticles.

## Preparation of hybrid chitosan-zinc oxide nanoparticles composite

Figure 1 directed that the appropriate amount of ZnO powder (0.5 wt%-2.0 wt%) was dissolved in100 mL of 1% (v/v) acetic acid. ZnO reacts with acetic acid and changed to zinc cations. It is proved that the solubility of chitosan decreases as the pH varies towards the basic condition, which is why chitosan and zinc oxide adsorbent were dissolved in acetic acid solution at pH less than 6.0. Over pH 6.0, it becomes insoluble in solution and exists as solid particles (Figure 5). Then 1.0 g of chitosan was added to the mixture solution. The mixture was sonicated for 30 min in sonicator bath. After magnetic stirring, 0.10 M NaOH was added drop by drop until the solution attained pH 7. The solution was heated in water bath at 75-80°C for about 3 hours. Next, the solution was filtered and washed with distilled water for several times before being dried in an oven at 50°C for 1 hour [5].



## Characterization of chitosan-zinc oxide nanoparticles composite

**FT-IR analysis of chitosan-zinc oxide nanoparticles:** Figure 2 illustrated that the IR spectra of chitosan showed a strong absorption band at 3309 cm<sup>-1</sup> due to OH and amine N-H symmetrical stretching vibrations. A peak at 2822 cm<sup>-1</sup> was due to symmetric -CH<sub>2</sub> stretching vibration attributed to pyranose ring [7]. A peak at 1134 cm<sup>-1</sup> was assigned to the structure of saccharine. The sharp peak at 1379 cm<sup>-1</sup> was assigned to CH<sub>3</sub> in amide group [8]. The broad peak at 1037 cm<sup>-1</sup> indicated the C-O stretching vibration in chitosan and peaks at 1641 and 1548 cm<sup>-1</sup> were due to -C=O stretching (amide I) and NH stretching (amide II). The absorption bands at 1134 cm<sup>-1</sup> was assigned to the anti-symmetric stretching of C-O-C Bridge.

Figure 2 shows the FTIR spectrum of the ZnO nanoparticles synthesized by sol-gel method, which was acquired in the range of 400-4000 cm<sup>-1</sup>. The band between the 450-500 cm<sup>-1</sup> correlated to metal oxide bond (ZnO). From this FTIR we can also observe that increasing the annealing temperature sharpens of the characteristic peaks for metal oxide, suggesting that, the crystalline nature of ZnO increases on increasing the calcinations temperature. The peaks in the range of 1400-1500 cm<sup>-1</sup> corresponds to the C=O bonds. The adsorbed band at 1548 cm<sup>-1</sup> is assigned O-H bending vibrations. The peak at 1379 cm<sup>-1</sup> and 1502 cm<sup>-1</sup> corresponds to C=O and O-H bending vibrations respectively diminishes gradually for sample annealed at higher temperature [5].

#### Treatment of colored effluents by composite

In each experiment, 20 ml of sample effluent was taken in a beaker and heated on a hot plate until the desired temperature level was reached. Then a definite preweighed amount of Composite was added to the hot effluent sample, stirred well and kept for a certain period of time. After that, the effluent sample was filtered using Whatman 44 filter paper. The obtained filtrate was allowed to cool to room temperature and analyzed in the UV-Vis. Spectrophotometer (Specord 205-Analytik jena) as per method described in section.

## Measurement of color intensity of effluents by spectrophotometric method: Computation of calibration curve

At first color intensity of the effluents was measured by a spectrophotometer (Specord 205-Analytik jena) against ultra-pure water. At a definite wavelength (i.e. 511 nm for colored effluent) maximum absorbance of the effluents was obtained. Color intensity of the original effluents was arbitrarily taken to be 100 units and calibration curve from the data given in the Figure 6 was made as shown in the Table 1 by diluting the original effluents, color intensity being taken to be equal to the percentage of original effluents in diluted

sample. The final concentration of dye was estimated with the help of these absorbance data. For determining the uptake of the dye, all-inclusive sets of experiments were performed at different time intervals (15, 30, 45, 60 and 75 minutes) and pH (2-9) etc. A range from 0.5 g to 2.0 g of adsorbent was also used to perform this experiment. The amount of adsorption at equilibrium time,  $q_e(mg/g)$  was calculated using equation:

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$$q_{\rm e} = (C_{\rm o} - C_{\rm e}) \,\mathrm{V/W}$$

Where,  $C_0$  for the liquid-phase concentrations of dye at initial (mg/L);  $C_e$ , for the liquid-phase concentrations of dye at equilibrium (mg/L); V represents the volume of the solution, (L); W=mass of dry adsorbent used, (g).

#### Data for calibration curve for effluent

Calibration curve for effluent was described in Table 1.

#### **Result and Discussion**

#### Effect of time of contact on color removal

Each 20 ml of the sample effluent was treated with 0.04 gm of composite for 50°C at various contact time as per method 2.4. Effects of contact time on adsorption were studied and results are shown in Figure 4. Figure shows that, increase in removal efficiency with increase

Serial No.	Color unit	Absorbance
1	100	0.1996
2	90	0.1773
3	80	0.1548
4	70	0.1357
5	60	0.1147
6	50	0.0967
7	40	0.0838
8	30	0.0583
9	20	0.0346
10	10	0.0128

Table 1: Data for calibration curve for Red effluent.





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Figure 8: Decolorization process with the increasing amount of Composite in Red effluent.

in contact time between adsorbate and adsorbent. It can be mentioned to the fact that more time becomes available for the dye to make an attraction complex with Composite (Figure 7).

The graph shows that, initial removal occurs rapidly as soon as the dye and composite in contact but after that when some of the easily available active sites engaged, dye needs time to find out more active sites for building. So, removal percentage is increased steadily over the period of experiment. It is concluded that dye and composite should be in contact for 60 minutes in order to get maximum removal percentage.

#### Effect of temperature on color removal

Each 20 ml of the sample effluent was treated with 0.04 gm. of composite for 60 minutes at various temperatures as per method 2.4.

From the results of the experiment it may be observed that decolorization of effluent by Co mposite was in fluenced by temperature. However, considering the extra cost (energy) involved at high temperatures and other difficulties encountered (e.g. evaporation, handling etc.) an optimum temperature of 50°C may be adopted for further investigation of the process for Hybrid Composite.

#### Effect of composite loading on color removal

Each 20 ml of the sample Red effluent was treated with increased amount of composite at a fixed temperature of 40°C for a definite time of contact of 10 minutes as per method described in section 2.4. The results are shown in Figure 6.

It is observed from the Figure 4 that removal of color from the effluent increases with increasing composite doses. It was also observed that color adsorption will be maximized if we take small amount of Composite such as 1.0 gm.

#### Effect of turbidity on red effluent

It may be seen from the results of the experiment that turbidity becomes lower with the increase of Composite loading. The effluent becomes apparent with the increasing amount of Composite (Figure 8).

Here it was found that the color of the effluents is decreasing with the increasing amount of Composite loading.

#### Conclusion

Batch adsorption studies of color removal from effluents of Textile dyeing industry were carried out using the above Chitosanzinc oxide nano particles composite. Three different samples of colored effluents were studied: Thus it may be concluded that, Chitosan-Zinc Oxide nano particles Composite has been successfully employed for removal of red color of the given effluent. Using 2 gm of Composite per liter of effluent at ambient temperature (50°C) and 60 minutes time of contact, it may be possible to remove 99% of the original color of the effluent. It has been shown that in general, an increase in temperature and contact time of solution facilitates greater color adsorption by composite. Color adsorption increases with the increase of the dosage of composite.

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