Removal of Cationic Dye from Textile Industry Wastewater with Using Enzyme, Fungus and Polymer

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Abstract: It was used significant amount of water in various processes such as dyeing, desizing and bleaching in textile industry. Thus companies have to be faced wastewater problems. Especially in dyeing process different type of colourants -for instance acidic, reactive, basic, disperse, azo, diazo, antraquionone- based and metal complex based - were applied to textiles and as a result it was obtained a huge amount of colourful wastewater from dye process. Due to treatment for these colourful wastewaters it can be applied many different methods such as adsorption, chemical oxidation, coagulation, membrane filtration. In this study, decolorization of cationic dye (Basic Blue 41) from local textile mill was investigated by using Horseradish peroxidase enzyme and sulfonated polymers at different pHs. In addition, removal of the cationic dye also carried out by using *Trametes versicolor* from white root fungus for pH 3,6. Decolorization effiency was high (90 %) with *Trametes versicolor* for 7 days, whereas little decolorization was observed with Horseradish peroxidase enzyme. It was achieved quicker total treatment of cationic dye with using sulfonated polymers in comparison to enzyme and fungus.

Key words: Cationic dye, Horseradish peroxidase, Trametes versicolor, decolorization, sulfonated polymer, adsorption.

Introduction

The textile industry consumes huge volumes of water in different wet processes and as a result it was obtained significant amount of colourful wastewater from dye process. In dying process, various dyes can be used such as acidic, reactive, basic, disperse, azo, diazo, antraquionone-based and metal complex dyes according to fabric types (Tuba et al., 2010).

Dyes present a potential human health risk as some of them have been shown to be carcinogenic. Traditionally wastewater treatment methods can be classified as physical, chemical and biological. Various chemical and physical methods, such as chemical coagulation and adsorption on activated carbon, are being used. However, these traditional methods mainly transfer the contaminants from wastewater to solid wastes, which may lead to a new kind of pollution (Chen and Zhu, 2007; Harazona et al., 2003; Onder et al 2011, Gupta and Suhas, 2009; Crini, 2006).

Medium-size factories can prefer physical and chemical techniques by using coagulants and/or floculates because of economical concerns. However, in spite of biological methods are more complex and unfortunately costly ways, they are most convenient and efficient methods, because total treatment of wastes can be achieved. In addition, to get good results/total treatment and cheapening of costs, various methods can be used together according to characteristic of wastewaters. These combining methods are useful and eligible for non-profit public purposes especially municipalities.

The use of enzymes is currently a possibility for application in environmental engineering, however their purification procedures are too expensive. Enzymes from various sources (fungus and plant based) have been applied for the treatment of dye based compounds. Fungal extracted enzymes have been mostly studied in dye removal processes (Chen and Zhu, 200); Onder et al, 2011; Harazona, 2003).

Table 1: Treatment of some basic dyes by using different methods

Dye/Solution	Method	References
Basic red 46	Electrocoagulation	Daneshvar et al., 2006
Basic Yellow 28	Electrocoagulation	Daneshvar et al., 2006
Basic dye textile effluent	Electrocoagulation	Zaroual et al. 2006
Basic Red 46	Photocatalytic (immobilized TiO_2 nanoparticles)	Khataee, 2009
Crystal violet	Adsorption (activated carbon)	Prasad et al., 2012
Methylene blue	Biosorption (*Trichoderma viride* fungus)	Asma et al 2009
Methylene blue	Superabsorbent hydrogel	Alexander, 2006
Crystal violet, Bismarck brown Y	Adsorption (modified chitosan)	An-Chong Chao et al., 2004
Methylene blue	Lignin peroxidase enzyme	Viridiana et al., 2007
Methylene blue	Adsorption (Hydrogels)	Bajpai et al., 2012
Basic violet 3 Basic red 9	*P. Ostreatus, S. Commune, S. Rolfsii, N. Crassa, Polyporus sp., T. Villosa and M. Thermohila*	Elias et al., 2000
Crystal violet, Basic fuchsin, Brillant gren, Malachite gren	Aeromonas hydrophila strain DN322	Ren et al., 2006
Methyl violet	Adsorption (perlit)	Mehmet and Mahir, 2003

Basic dyes are cationic soluble salts of coloured bases. Basic dyes are applied to substrate with anionic character where electrostatic attractions are formed. Basic dyes are powerful colouring agents. It's applied to polyacrylonitrile, modified nylons, modified polyesters, paper. They are generally water soluble (Gupta and Suhas, 2009).

In the present work, an attempt has been made to examine the efficiencies of various waste treatment methods (enzyme based, microorganism based and polymer based) for colour (Basic Blue 41) removal at different conditions.

Materials and Method

The cationic dye were provided from a local textile mill. Horseradish Peroxidase (E.C. 1.11.1.7) (Mw ~ 40.000 Da) (Fluka), D (+) glucose (Fluka), malt extract (Merck), acetic acid (Fluka), sodium phosphate dibasic (Riedel-de Haen), monobasic sodium phosphate (Riedel-de Haen) and Trametes versicolor were analytical reagent grade and used as received without further purification. In all experiments ultra pure water was used obtained from Millipore MilliQ system. Sulfonated polymers that used in experiments were obtained from Du Pont or synthesized in our lab (Kaya, 2012).

Removal of Basic Blue 41 by Horseradish Peroxidase

Decolorization of Basic Blue 41 (B 41) dye using Horseradish peroxsidase was carried out directly in the spectrophotometer cuvette. The reaction was started by adding buffer solution at different pHs, B 41 dye, HRP enzyme and finally H_2O_2 (3 %) as the initiator in the reaction cuvette (Onder et al, 2009). The final volume of the reaction cuvette was 3.0 mL. Dye decolorization was measured with temperature controlling UV-Vis spectrophotometer (Model UV–1700 Pharmaspec Shimadzu) based on the maximum absorbance at 608 nm in the visible range, at different pHs (5.0, 6.0, 7.0, 8.0) and 30 ^{o}C temperature.

Removal of Basic Blue 41 by *Trametes Versicolor* from White Root Fungi

Culture Medium and conditions: *Trametes versicolor* Strain T (DSM 11309) was maintained on 2% (w/v) malt agar plates. Three cubes of 0.5 × 0.5 cm were transferred to 500-mL Erlenmeyer flasks, which contained 150 mL liquid medium (25,0 g malt extract, 2,0 g KH_2PO4, 0.4 g K_2HPO4; deionized H_2O ad. 1,000 mL, pH 5.5) and were grown in static culture for 14 day under at 30 ^oC (Borchert and Libra, 2001).

Media for dye decolorization: 2,50 g malt extract and 0,10 g glucose dissolved in 100 mL deionized H_2O then pH was adjusted to 3,6 and sterilization at strilazator for 15 min. at 1,2 atm and 121 ^oC (Borchert and Libra, 2001). All steps were performed aseptically with sterile media.

Removal of Basic Blue 41 by Sulfonated Polymers

Basic blue 41 dye was prepared in distilled water. The pH of dye solution was adjusted with 0.1 N NaOH and HCl solution. The pH of solutions was measured with a pH meter. The study was performed in 15 mL tubes with a working volume 5 mL of dye solution different pHs. Tubes were placed in on shaker at 300 rpm at room temperature.

Results and Discussion

Dye decolorization values were calculated according to decreasing of maximum absorbans (608 nm)of the basic blue 41 dye at different incubation times (Figure 1).

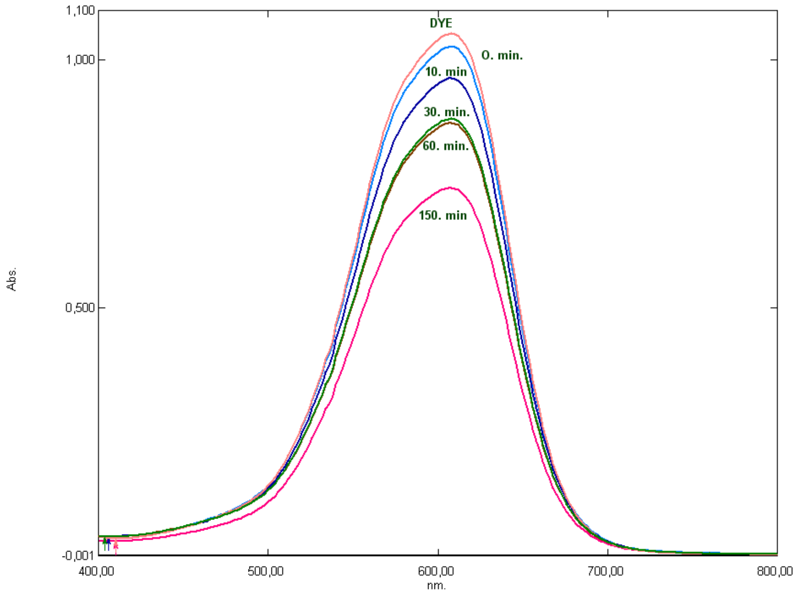

Figure 1: Decolorization of Cationic (basic) dye B 41 by using Horseradish Peroxidase enzyme at pH: 7.0 and 30 ^0C for different incubation time.

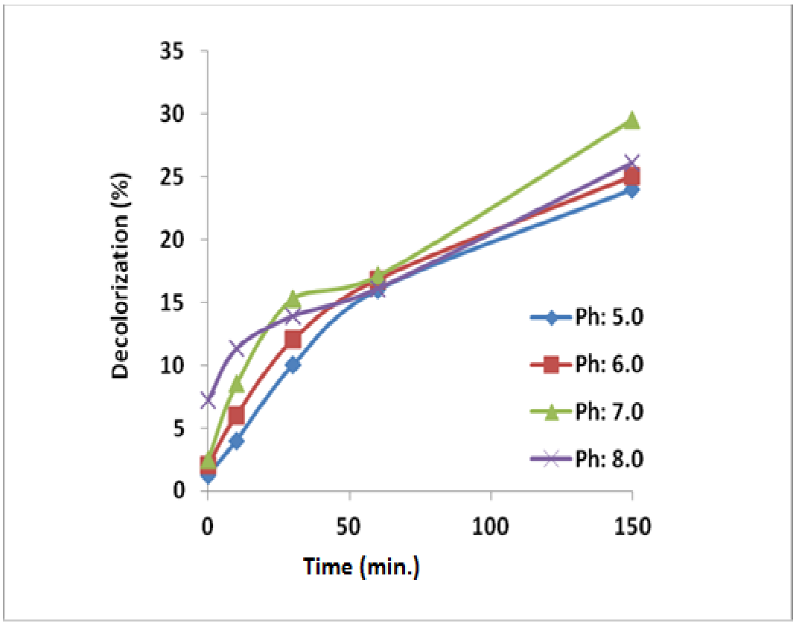

Figure 2: Decolorization (%) of Cationic (basic) dye B 41 by using Horseradish Peroxidase enzyme at different pHs and 30 ^{0}C.

In our previous study, acidic pHs were more effective for decolorization of Naphtol Blue Black (acid dye). Optimum pH of the Horseradish peroxidase enzyme was 5.0 for decolorization of acid dye (Onder et al, 2011). In this study, decolorization values of basic dye was low according to our previous study (acid dye) with the Horseradish Peroxsidase enzyme.

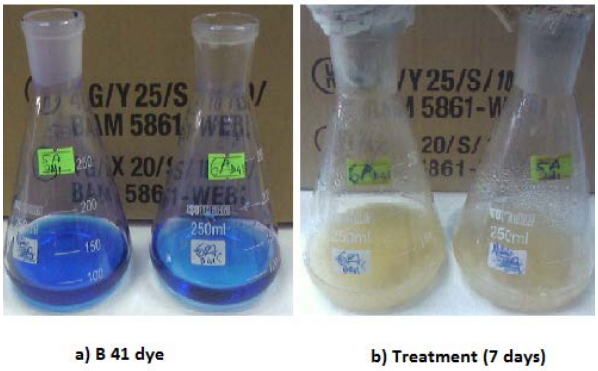

Figure 3: Removal of B 41 dye by using Trametes Versicolor from White Root Fungi at pH: 3,6 and 30 ^{o}C.

B 41 dye was removed 90 % after 7 days by using Trametes Versicolor from White Root Fungi. The microorganism was high removal values at acidic pHs. For this, it was studied at pH: 3,6. Decolorization of Basic Blue 41 was continued for 7 days under shaking conditions at 30 ^{0}C and pH 3,6 using Trametes versicolor from White root fungi.

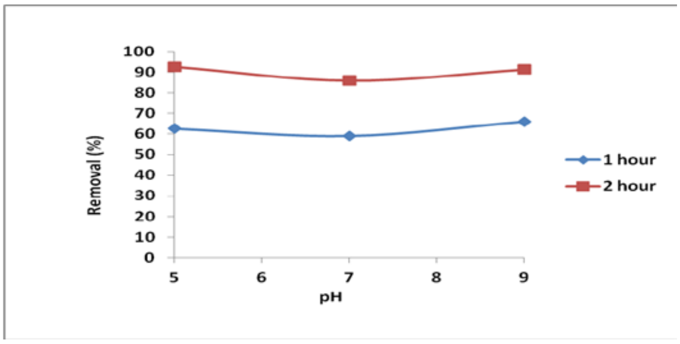

Figure 4: Removal of Basic Blue 41 by using commercial sulfonated polymer at different pHs.

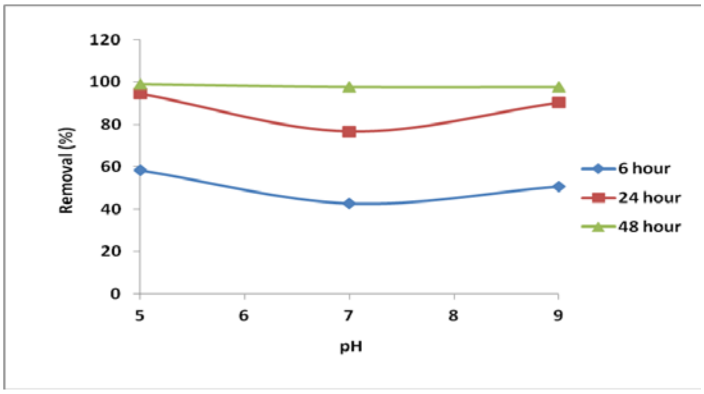

Figure 5: Removal of Basic Blue 41 by using our synthesized sulfonated polymer at different pHs.

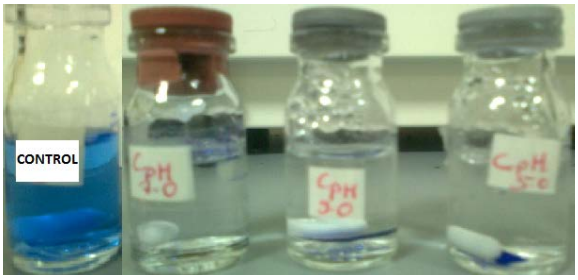

Figure 6: Removal of Basic Blue 41 by using commercial sulfonated polymer after 3 hour.

Figure 7. Removal of Basic Blue 41 by using our synthesized sulfonated polymer after 6 hour.

Sulfonated polymers can easily and quickly adsorp cationic dyes due to carrying structural negative charges. Both sulfonated polymers (commercial and synthesized) exhibit superior removal efficiency relatively in a short time in comparison to other methods (enzyme based and microorganism based). In view of total treatment time, it has to be noted commercial sulfonated polymer is quicker than synthesized sulfonated polymer.

Conclusions

In the light of experiments, results can be summarized following;

- Dye removal process from wastewaters is strictly depend on pH value.
- Synthetic dye solutions were decolorized in short time (2 h.) by commercial sulfonated polymer. On the other hand our synthesized sulfonated polymer removed dyes after 2 days.
- Decolorization effiency was high (90 %) with *Trametes versicolor* for 7 days, whereas little decolorization was observed with Horseradish peroxidase enzyme.
- Using sulfonated polymers is most convenient and efficient method in among other methods for decolorization of the cationic dye, because of their shorter treatment time and high efficiency.

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