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GC-MS and Spectrophotometric Analysis of Degradation of Commercial Textile Dye Reactive Black CNN by Advance Oxidation Processes

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Abstract. This study evaluates the efficiency of Fenton processes which are one of advance oxidation processes for degradation of reactive black CNN from aqueous dye solution. Samples were treated with Fenton's, photo and Fenton's like reagent to check and compare % decolourization efficiency of the processes. Optimization of different operating parameters like dose of dye, concentration of H_2O_2, concentration of iron salts, contact time and temperature has been determined. Results showed that the overall degradation of Reactive Black CNN was much faster by photo Fenton oxidation process as compare to Fenton or photo Fenton like oxidation. For the three oxidation systems, the percentage color removal efficiency depends on [Dye], [Fe_2+], [Fe_3+], [H_2O_2], temperature, contact time and sun light exposure time.

Keywords: reactive black CNN, degradation, UV-visible spectral analysis, COD, GC-MS

Introduction

Textile industry utilizes water on larger scale and is the biggest consumer of colouring agent in dying finishing and printing processes. These industrial processes from printing and dyeing units release effluents with higher concentration of chemical compounds which are extremely colourized having diverse chemical mixtures (Chacon, 2006).

Textile wastewater contaminants are common detergents, caustic soda, inhibitor compounds, toxic materials, chlorine compounds (AOX), active substances, pH altering substances, salt and dying substances wax, starch, urea, pigments, ammonia and dyes that increase its COD, BOD solid residues and ultimately the harmfulness. This water with chemical nuisances must be treated properly before its discharge into the surrounding water bodies or in nearby open places (Ghosh *et al*., 2000).

Textile industry is putting a lot of pressure in environmental resources by consuming large amount of water and by releasing emissions consisting of chemical mixtures and colour dyes which are being used in various industrial units (Naseer *et al*., 2016).

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In, Pakistan the textile industry has higher contribution in economy and this industry uses huge amount of water. As water is shrinking source, so it is necessary for textile waste water to be treated with most promising treatment methods before its discharge into water bodies. The wide variety of dyes are used in textile manufacturing procedures but most frequently used dyes are azo dyes which consist of 80% reactive dyes. Reactive dyes are used at larger scale because of their advantages as they can be applied at slight operating conditions, produce light colours, have stable structures, depict excellent wet-fastness and their dying procedure is easily applicable (Wang *et al*., 2002). Reactive dyes are one of the group of azo dyes which are classified based on azo bond (N=N) and this is used for dying the cellulosic fibres (Al-Degs *et al*., 2000).

There are various conventional ways of removing these dyes from waste water by different methods for example activated sludge treatment, carbon adsorption, flocculation, membrane filtration and reverse osmosis. But these methods are incompetent and have many other drawbacks for production of secondary pollutants. (Malik, 2003). Different methods are available for the treatment. In recent times, many other evolving processes, recognized as advanced oxidation processes have been used with satisfactory results for the pollutant eradication in industrial waste waters. These processes are based on the production of radical with high very high oxidizing power such as hydroxyl radicals. Among all methods Advance Oxidation Processes (AOPs) are considered as highly effective physico-chemical treatment methods because of their application feasibility and ability to show significant changes in the chemical structures of the pollutants by the using free radicals which are strong oxidizing agent (Oturan *et al*., 2008). These methods depend on the formation of radical having high oxidation potential as $\dot{O}H$ radicals having oxidation potential of 2.8V (Qiang *et al*., 2003).

Pakistan's economy heavily relies upon textile industry. As stated above, the large consumption of water is major concern. Water is non-renewable and decreasing source, so it is essential for textile industries to treat the waste water with most efficient and effective treatment methods before it is being discharged in surrounding atmosphere (Kiran *et al*., 2013).

In this investigational study Fenton's reagent (Fe^{2+} + H_2O_2) alone and with UV exposure was used to eliminate reactive black CNN (used as model dye) from synthetic aqueous solutions. Influence of using Fenton's reagent alone and with exposure of UV was investigated and compared for the removal of dye from textile waste water at larger scale.

Materials and Methods

Materials. Model dye used in present study was reactive black CNN. Samples of reactive black CNN were made in the laboratory.

Experimental procedures. The present study was conducted to check the efficiency of Fenton's reagent along with H_2O_2 in presence of UV and in absence of UV for the removal of reactive black CNN from waste water on lab scale. Removal was done by $FeSO_4$, $FeCl_3.6H_2O$ and H_2O_2 under shaking condition of 15 min with UV using sunlight and without UV. Optimization of different operational parameters, which are supposed to affect the colour removal was also carried out. All the chemicals used during research work were of lab scale with 85% and above purity. Various solutions of dye with different concentrations *i.e*. 10, 20, 30, 40 and 50 ppm were prepared by stock solution (100 g/L). Stock solution of dye was prepared by taking 0.025 g in 250 L of tap water and then diluted to get desired dye concentrations and absorbance of each dye solution was measured using spectrophotometer to find λ_{max} by using ultraviolet-visible spectrophotometer for calibration curve. To perform removal experiments Solutions of $FeSO_4$ were prepared in different concentration ranging (0.001, 0.002, 0.003, 0.004 and 0.005 M) with distilled water. Similarly various solution of H_2O_2 (100-500 ppm) were prepared with deionized water for optimization of H_2O_2 solution. These solutions were used to treat samples for dye removal. Then each experiment was repeated with UV exposure to compare efficiency of oxidation processes which were Fenton's (Fe^{2+} + H_2O_2), photo Fenton's(Fe^{3+} + H_2O_2) and photo Fenton's (Fe^{3+} + H_2O_2+UV) like processes.

Analytical methods. By using UV/VIS spectrophotometer UV-Vis spectra of reactive black CNN solution were recorded from 200-800 nm. Water as a black was used in the experiments. The λ_{max} of reactive black CNN was found 600 nm. Absorbance of reactive black CNN solutions (10-50 ppm) was determined in each experiment at 600 nm and using a calibration curve.

Decolourization efficiency of reactive black CNN was calculated as:

$$\text{Decolourization efficiency} = \frac{\text{Initial abs. – final absorbance}}{\text{Initial absorbance}} \times 100$$

GC-MS (GCMS-QP2010 with FID detector and column 5MS) was used for the analysis to calculate extent of colour removal and to examine the chemical structure of degraded products.

Results and Discussion

Effect of dye dose. Experiments were conducted to check the effect of dye concentration on oxidation of sample aqueous solutions of reactive black CNN as quantity of pollutant is a vital factor. From results, it was evaluated that when concentration of dye was raised it showed significant effect on percentage colour removal as it was also studied by Moosovi *et al*. (2005). It was observed that dye was used in high concentration there was low difference in degradation proficiency of reactive black CNN by adopted processes. Whether by raising dye dosage (10-50 ppm) reduction in percentage colour removal of dye was observed. This revealed that when samples are treated with persistent amount of hydrogen peroxide and Fe^{2+}, more H_2O_2 is require due to high concentration of dye. The most likely reason may be that, as the concentration of reactive black CNN was raised. Further dye molecules were adsorbed by catalysts surface (Kiran *et al*., 2017 and 2012). But the additional adsorbed molecules were not degraded quickly since UV light and concentration of catalyst was constant (Neppolian *et al*., 2002). The decolourization efficiency by the dye is shown in Fig. 1.

Effect of time. To design an economical frame work to treat waste water time should also be considered as important limiting factor. To eliminate the pollutants, it is very considerable point to determine the optimum contact time of reaction which should be cost effective and should be enough to decompose the pollutants in less harmful compounds (Kiran *et al*., 2012a and b). Results of experiments revealed that the raised contact time showed positive effect on decolourization as on enhancing the reaction time percentage of colour removal was also raised which showed reaction time plays very significant role in degradation of reactive black CNN (Bigda *et al*., 1995). By comparing the effect of reaction time on colour removal in Fenton and photo Fenton oxidation, it would be analyzed that removal was highest when reaction time was of 60 min with UV exposure for these both above mentioned oxidation reactions as analogous results have been studied by Son *et al*. (2009). The reason of such behaviour may be that when solutions of sample dye exposed to ultraviolet (UV) rays for maximum time which raises the formation of $\dot{O}H$ free radical and this is also accelerates oxidation process (Ince *et al*., 1997). The decolourization efficiency by the time is shown in Fig. 2.

Effect of temperature. Commonly, changes in temperature show significant effects on many oxidation processes. That is why effect of temperature is important parameter to get a complete idea of chemical oxidation reaction (Liou *et al*., 2005). In this investigational study to examine the extent of colour removal, experiments were conducted on 25 and 50 °C. When temperature was raised from 25 to 50 °C both in Fenton and photo Fenton processes a considerable rise in decolouriation trend was observed. It is apparent from result's that by increasing temperature of oxidation reaction the time required for degradation of reactive black CNN can be reduced. The decolourization efficiency by the temperature is shown in Fig. 3.

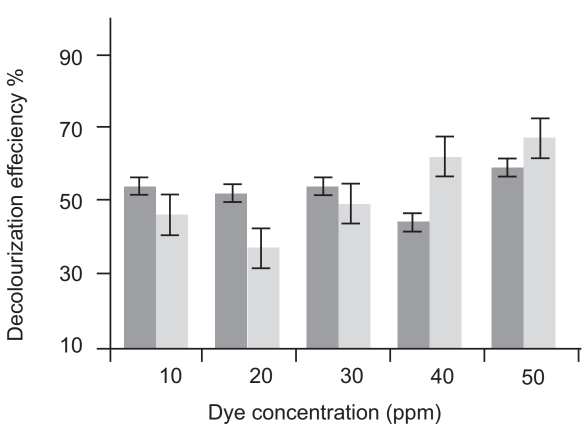

Fig. 1. Effect of dye concentration on decolourization by Fenton photo Fenton process (red is Fenton and green is Photo Fenton like).

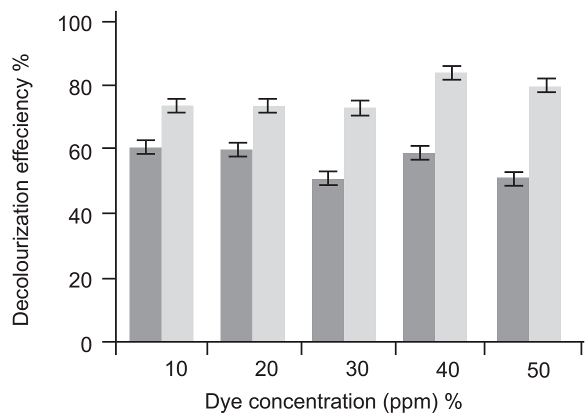

Fig. 2. Effect of contact time of 60 min on decolourization of dye by Fenton and photo Fenton reaction (red is Fenton and green is photo Fenton like).

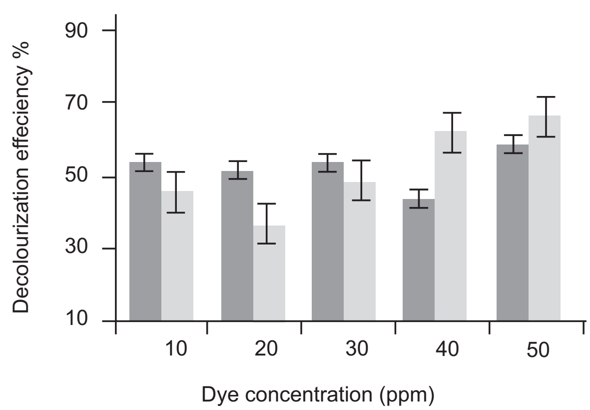

Fig. 3. Effect of temperature (50 °C) on decolourization of dye by Fenton and photo Fenton reaction (red is Fenton and green is photo Fenton like).

Effect of iron dose. Like the other parameters, concentration of iron is also taken as very significant factor in advance oxidation processes for efficient decolourization from the dye solutions as it is being used as a catalyst. That is why it is very crucial to optimize the iron concentration. This most important factor in oxidation reaction controls the oxidation potential with association of hydrogen peroxide at a given initial dye dosage. From conclusions it has been evaluated that by treating the samples with Fenton's reagent the percentage degradation of reactive black CNN was increased by raising the concentration of Fe^{2+}or Fe^{3+} from 0.001 to 0.005M. The less decolourization capability of Fenton's reagent at small dose of iron may be due to fewer production of hydrogen peroxide which is required for complete oxidation reaction of dye (Chatha *et al*., 2016; Lucas *et al*., 2006).

Effect of H_2O_2 dose. To check the efficiency of Fenton process and photo Fenton process for decolourization initial concentration of H_2O_2 was also observed. It is important factor as it is source of $\dot{O}H$ production which cause oxidation of dye. Results of experiment showed on raising the concentration of hydrogen peroxide proficiency of the oxidation for colour removal processes had enhanced also along with raising the amount of ferrous as well. The increased rate of colour removal is due to high formation of $\dot{O}H$ radicals when more concentration of H_2O_2 is added. The higher decolourization by photo Fenton process is due to enhanced formation of hydroxyl radical by exposing the samples with UV rays. These free radicals are absorbed by dye and that is why higher decolourization is achieved than decolourization by Fenton process. It was also evaluated that at higher concentration of hydrogen peroxide. It exhibits scavenging properties which cause deactivation of hydroxyl radical and drops its reactivity as it also has been studied by Devi *et al*. (2009). The decolourization efficiency by the concentration of H_2O_2 and Fe^{2+} is shown in Fig. 4.

Effect of Fe^{3+} in Fenton like and photo Fenton like oxidation. After treating samples with Fenton reagent and photo Fenton reagents they were treated with two more reagents respectively *i.e*. Fenton's like reagent ($Fe^{3+} + H_2O_2$) and with photo Fenton's like reagent ($Fe^{3+} + H_2O_2$+UV) using 0.005M concentration of Fe^{3+}, shaken for 15 min on agitator at 25 °C. It was found that the decolourization efficiency of reactive black CNN by photo Fenton like reagent was higher as compare to Fenton like reagent. The effect of Fenton like and photo Fenton like oxidation on decolourization of reactive black CNN is shown in Fig. 5 and decolourization efficiency of photo Fenton and photo Fenton like oxidation is shown in Fig. 6.

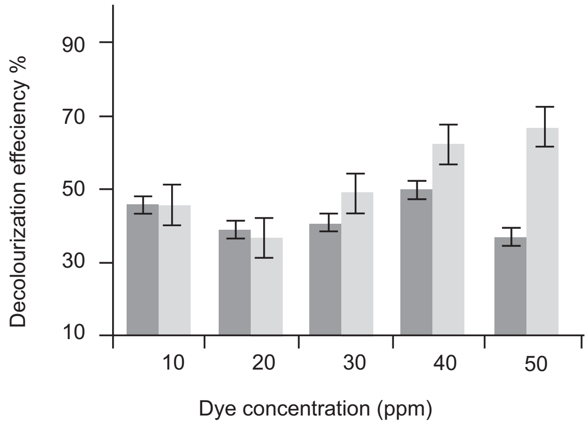

Fig. 4. Effect of temperature (50 °C) on decolourization of dye by Fenton and photo Fenton reaction (red is Fenton and green is photo Fenton like).

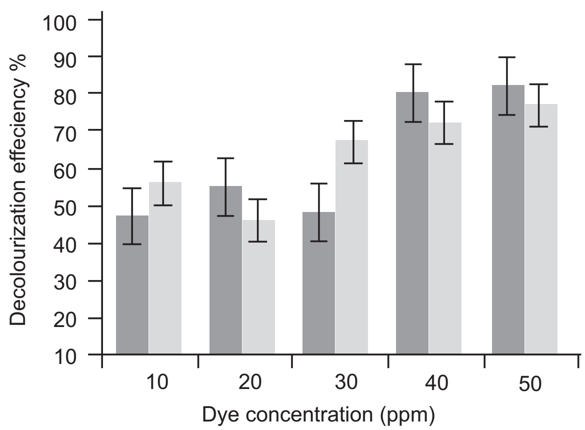

Fig. 5. Effect of Fenton like and photo Fenton like oxidation on decolourization of reactive black CNN (red is Fenton and green is photo Fenton like).

UV-VIS Spectra of the reactive black CNN oxidized by Fenton processes UV-visible spectroscopy of samples was done to check the rate of decolourization of model dye in synthetic aqueous solutions. UV-visible spectrum of untreated reactive black CNN was consist of two major distinctive adsorption bands. One band was in the UV region (300 nm) and the other band was in the visible region (600 nm). UV band represents two adjacent rings, however visible band possess two long conjugated bond associated by two azo groups (Kiran *et al*., 2013; Silverstein *et al*., 1991). On the other hand, in visible region (600 nm) absorption peaks were vanished completely in spectrum of all treated dye samples which showed complete decolourization of reactive black CNN.

GC-MS Analysis. GC-MS analysis of samples treated with all oxidation processes was conducted by using GC-MS. GC-MS analysis of dye samples showed when model dye reactive black CNN having molecular weight of 991.82 was treated with Fenton's, photo Fenton's and photo Fenton's like processes, there were several peaks but there was no indication of development of any dangerous aromatic amine in all treated samples.

Chemical oxidation demand. Chemical oxidation demand defines the total amount of oxygen required to eliminate the organic matter existing in any sample by method of oxidation using some oxidizing chemicals which have significant oxidizing capability. Experiments were performed to check the degradation level of model dye by calculating chemical oxidation demand COD. To check chemical oxidation demand we used the titration method. Result showed COD rate of dye was higher as compared to the COD value of treated samples, which exhibits proficiency of oxidation processes for removal of sample dye.

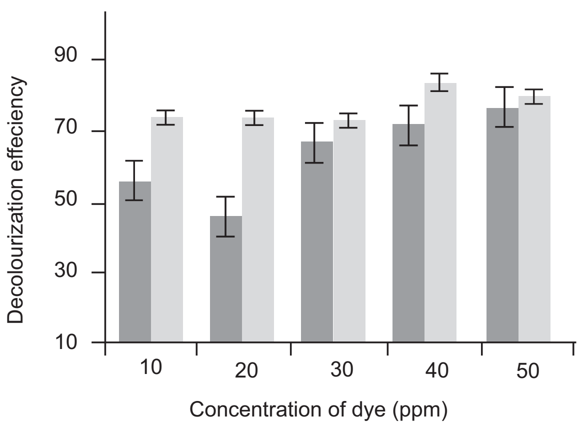

Fig. 6. Decolourization efficiency of photo Fenton and photo Fenton like oxidation (red is Fenton and green is photo Fenton like).

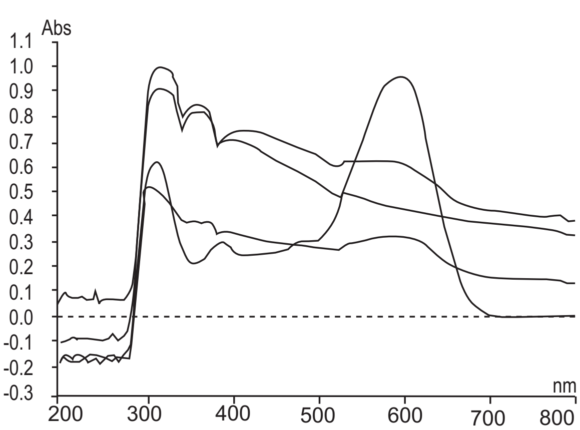

Fig. 7. UV-Vis overlaps spectra of untreated dye and treated samples with Fenton, photo Fenton and photo Fenton like reaction.

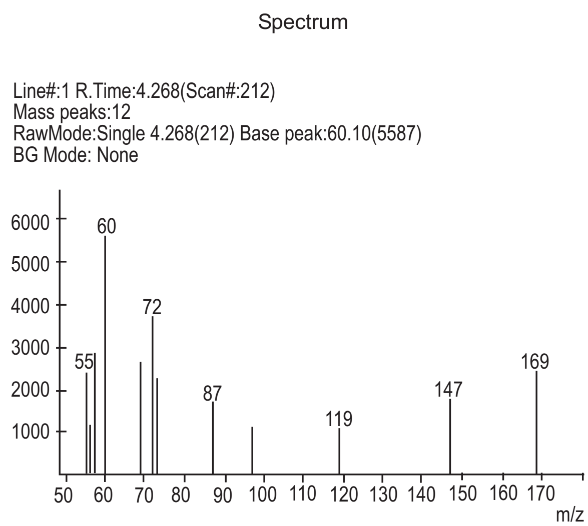

Fig. 8. GC-MS mass spectra of dye sample treated with photo Fenton's reagent ($FeSO_4$+H_2O_2 + UV).

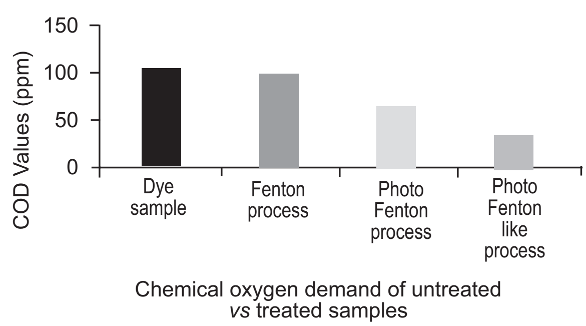

Fig. 9. Comparison of COD removal by different Fenton oxidation processes.

Conclusion

Fenton, photo Fenton and oxidation process with Fe^{3+} + H_2O_2 + UV can effectively decolourize the sample dye, reactive black CNN from synthetic samples by agitating samples for optimal time but it was also observed that decolourization rate was very high in photo Fenton process and photo Fenton like process as compared with simple Fenton oxidation process. On the other hand, it was also concluded that oxidation processes involving Fe^{2+} ions exhibit maximum decolourization proficiency as compared to Fe^{3+} ion to oxidize the sample dye. Order of oxidation efficiency of processes is UV+ Fe^{2+}+ H_2O_2 >Fe^{3+} +H_2O_2 +UV >Fe^{2+} +H_2O_2.

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Conflict of Interest. The authors declare they have no conflict of interest.

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