Full Length Research Paper

Comparison of various oxidative treatments for removal of reactive black CNN

Madiha Nisar, Sofia Nosheen*, Aqdas Noreen, Iram Majeed, Ana Saleem and Munir Ahmad Sheikh

Department of Chemistry and Biochemistry, University of Agriculture Faisalabad, 38000 Faisalabad, Pakistan.

Accepted 24 October, 2011

Decolorization of reactive black CNN by chemical oxidation and reduction using KMnO₄, H₂O₂ and Ferrioxalate as oxidizing agents and Na₂SO₃ as reducing agent individually as well as in combination was studied on batch scale using UV-visible spectroscopy. Degradation of dye occurred in acidic medium with KMnO₄ and in alkaline medium with H₂O₂ and ferrioxalate. The most efficient methods for decolorization of reactive black CNN is oxidation using KMnO₄ as an oxidizing agent which removed 97.64% of dye. Maximum decolorization was obtained at 60 min of treatment under static conditions. H₂O₂ and ferrioxalate could remove only 50.71 and 44.21% dye, respectively. Sequential treatment was more successful with H₂O₂ and ferrioxalate when compared with KMnO₄. Chemical oxygen demand (COD) and total organic carbon (TOC) contents of treated wastewater decreased appreciably from 83.6 to 63.7 mg/L and 86.8 to 72.8 mg/L, respectively. Additionally, Fourier Transform Infrared Spectroscopy (FTIR) study revealed the degradation of reactive black CNN after treatment into non toxic products.

Key words: Reactive black CNN, KMnO₄, ferrioxalate, sodium sulphite, chemical oxygen demand (COD).

INTRODUCTION

Industrial effluents from various industries like textile, dyestuffs, paper and pulp, distillery and metal industries etc. are the major contributors to water pollution as they create more subtle effects on behavior, reproduction or even survival of biotic communities (Styliki et al., 2003). Largest industrial production of wastewater is involved in dyeing processes. An effluent resulting from dyeing cotton fabric and rinsing sections shows some serious environmental issues as it carries too much color and is highly conductive because of presence of large amount of free dye molecules (Faria et al., 2004). Synthetic dyes containing azo functional group are more soluble in water and show a wide variety in colors. Their structures remain unaffected in most of the treatment methods which might be attributed to their complex aromatic structure and presence of substituents variable in nature (Pagga and Brown, 1986). Chemical oxidation method, however, appears to be the most potent technology for the treatment of wastewater of textile industry having reactive azo dyes (Yang et al., 1998). It is one of the most effective methodologies of expelling the contaminants out of the effluent and an excellent option for treatment, particularly when the oxidant is cheap and easily accessible.

Previously some researchers have performed a couple of experiments to study the color removal of various dyes (for example, acid red 73, acid red 14, acid orange 8 and acid orange 7). However, efficiency of oxidizing agents was variable (Aleboyeh et al., 2009; Salem et al., 2009).

Pakistan has textile based economy showing an urgent need for development of efficient treatment methods. The present study involved application of chemical oxidation and reduction methods for decolorization of reactive black CNN, model dye, using various oxidizing agents (KMnO₄, H₂O₂, and Ferrioxalate) and reducing agent (Na₂SO₃). Combined effect of reducing agent with each oxidizing agent was also analyzed for comparing efficiency of these methods currently employed for the treatment of colored wastewater on large scale in
European countries.

MATERIALS AND METHODS

Synthetic effluents of concentrations ranging from 10 to 100 ppm were prepared from stock dye solution for determination of \( \lambda_{\text{max}} \) of reactive black CNN. Each solution was individually treated with all oxidizing agents, reducing agent and sequentially with reducing and oxidizing agents to find out at which concentration maximum dye was decolorized. Optimized concentration of dye was used to determine the optimum pH value required for degradation of dye. pH was fixed up by adding diluted \( \text{H}_2\text{SO}_4 \) acid and diluted NaOH base.

Individual treatment with reducing and oxidizing agents

The synthetic dye solutions were treated with \( \text{KMnO}_4 \), \( \text{H}_2\text{O}_2 \), ferrioxalate and \( \text{Na}_2\text{SO}_3 \) in 1:1 ratio at various experimental conditions. Dye solution and solution having reacting species were mixed well in equal quantity and placed in static position. Same set of experiments were run under shaking conditions. At regular intervals of 30 min, aliquots were withdrawn for spectroscopic analysis to monitor dye decolorization. In case of \( \text{KMnO}_4 \), 100 µl of 1 M hydroxylamine hydrochloride (\( \text{NH}_2\text{OH.HCl} \)) solution was supplemented to the treated solution before taking absorbance as it eliminate permanganate interference (Aleboyeh et al., 2009). Ferrioxalate was prepared by dissolving the solutions of hydrated ferric ammonium sulphate and dipotassium salt of oxalic acid in 1:3 proportionality. Recrystallization of resultant ppt was carried out, filtered and dehydrated at 60°C for 24 h. Complex formed in this way was saved in a brown bottle to keep it safe from light reactions (Hatchard and Parker, 1956).

Sequential treatment with reducing and oxidizing agents

Reduction and oxidation methods exercised above were joined together to check their effect on color removal. Each dye sample was initially treated with reducing agent and then same solution was passed through oxidizing environment using oxidizing agents separately. A double beam UV-visible spectrophotometer (BMS 2600) was used for decolorization assay. The decolorization efficiency was calculated by using following formula:

\[
\text{Decolorization efficiency} \ (\%) = \left( \frac{A_{\text{initial}} - A_{\text{final}}}{A_{\text{initial}}} \right) \times 100
\]

\( A_{\text{initial}} \) = Absorbance before decolorization

\( A_{\text{final}} \) = Absorbance after decolorization

Degradation of reactive black CNN was also checked by measuring chemical oxygen demand (COD) and total organic carbon (TOC) of synthetic effluent before and after treatments by standard methods (Greenberg et al., 1993; Clesceri et al., 1998) with slight modifications.

Finally, Fourier transform infrared spectroscopy analysis was performed to get information about chemical changes that have occurred during these chemical treatments based on Redox reactions.

RESULTS AND DISCUSSION

Effect of dye concentration

Effect of dye concentration on decolorization rate was evaluated at 10 to 100 ppm concentration. The \( \lambda_{\text{max}} \) of reactive black CNN was confirmed to be 600 nm. Figure 1 to 3 shows effect of dye concentration on color removal in different treatment methods under static and shaking conditions separately. With \( \text{KMnO}_4 \), 72.73% of color removed in solution with10 ppm initial concentration which went on increasing with increase in concentration and reached to a maximum value of 97.64% in 100 ppm dye solution. The color reduction efficiency increased on increasing the amount of dye in reaction mixture. As the chance of interaction of organic contents with oxidizing molecules extends with increasing amount of dye so color removal content would be increased (Aleboyeh et al., 2009; Salem et al., 2009). When decolorization was carried out with \( \text{H}_2\text{O}_2 \), 40% color removal was observed in solution having 30 ppm initial concentration. Efficiency decreased to 27% in 100 ppm solution on further increase.
in concentration. On increasing amount of dye, degradation rate enhanced due to an increase in dye and free radical connection resulting in enlarged color removal ability. But adding more dye to the medium decreased the percent color reduction instead of enlarging it. It may be due limited accessibility of the oxidant to dye molecules. Similar results were also reported by some researchers previously (Salem et al., 2009). Decolorization obtained by ferrioxalate was showing trend similar to the one observed with \( \text{H}_2\text{O}_2 \).

Ferrioxalate alone when used as oxidizing agent (Figure 1) could not give promising results and only 35% dye could be removed (Park and Choim, 2003). Keeping in view \( \text{H}_2\text{O}_2 \) alone as oxidizing agent, only 40% dye removal could be achieved which is negligible to be used on large scale. Therefore, neither \( \text{H}_2\text{O}_2 \) nor ferrioxalate effectively reacts with dye when added individually (Salem et al., 2009).

**Effect of reaction time**

Better decolorization results were obtained with KMnO\textsubscript{4} at longer reaction time. However, in case of \( \text{H}_2\text{O}_2 \) and Ferrioxalate, the decolorization efficiency decreased on increasing time. The oxidizing agent can be utilized by some intermediary compounds produced during degradation process of dye, interfering in decomposition.
of compound under consideration thus retarding the whole process. The deficiency of oxidizing species in reaction media due to its continuous use can also be a reason of decline in reaction process. A reaction time of 60 min was considered most appropriate for experimentation. Effect of time on decolorization in various experiments is expressed in Figure 4.

**Effect of pH**

On treatment with KMnO₄, Redox potential of the medium effectively changed due to change in pH thus making it an influential parameter. Mechanism of the oxidation process can be explained in both acidic and basic media. However, rate of reaction depends upon the chemical specie under reaction. The maximum decolorization (98.44%) was obtained at pH 1.5. Decolorization efficiency was reduced critically to 61.74% at pH range between 2 to 4. At pH greater than 4, color of the reaction mixture was not pretty much removed. Similar results were observed in literature studied (Xu et al., 2005; Aleboyeh et al., 2009) who reported higher oxidation rate of KMnO₄ (for dye decolorization) at acidic pH. Further experiments with KMnO₄ were performed at pH 1.5. Oxidation with H₂O₂ is also strongly influenced by pH which affects the amount of hydroxyl radical generation (significant specie in degradation process) at various pH values. In present study discoloration reaction with H₂O₂ was moving very slowly at pH less than two (Figure 5). It may be because of the increased stability of hydrogen peroxyde as a result of hydronium ion formation which also diminished the free radical generation in acidic environment. On increasing the pH, rate of oxidation reaction increased progressively. The maximum decolorization value (34.03%) was obtained at pH 12. Less color reduction in acidic medium is probably due to the free radical scavenging process of hydrogen ions (Peres and Lucas, 2006; Sun et al., 2007). Ferrioxalate also achieved maximum degradation of dye wastewater at pH 12. At pH 1-2, a very slow decolorization process was observed. By increasing the pH up to alkaline medium increase in decolorization tendency was witnessed.

Optimum pH for both H₂O₂ and ferrioxalate was found to be 12 as cleared from data. Improvement in oxidation process in basic media is possibly for the reason that hydroxyl anions exist extensively at higher pH range, promote the free radical production which make degradation of dye easy (Kansal et al., 2007; Salem et al., 2009).

**Effect of oxidizing agents**

Degradation efficiency of KMnO₄, H₂O₂ and ferrioxalate was investigated individually both under static and shaking conditions. It was observed that KMnO₄ removed dye more efficiently in static media as compared to under continuous shaking condition. Chemical structure of dye and impact of intermediary compounds formed during degradation process plays an important role in decolorization. Azo dyes contain N=N bond in their structures along with aromatic rings of various kind which acts as a functional group and color causing part of dye (Muruganandham and Swaminatham, 2004). The quantity of KMnO₄ needed to remove all kind of azo dyes can vary in accordance with the sum of color causing
Effect of sequential treatment of reducing and oxidizing agents

Combination of $\text{H}_2\text{O}_2$ with sodium sulphite makes it more potent for degradation of dye, as shown in Figure 3. In static mode, maximum decolorization of 62.19% was achieved in 40 ppm concentrated solution. Effect of ferrioxalate combined with $\text{Na}_2\text{SO}_3$ was compatible with $\text{H}_2\text{O}_2$. Ultimate decolorization of 75.93% was achieved by dye solution of 30 ppm concentration in static medium. After that color removal efficiency decreased gradually with increase in dye concentration. The process of decolorization equipped with shaking could enhance the interaction of dye with reacting compound. Therefore, increased color reduction on shaking is estimated because of greater dye association with oxidizing and reducing compounds (Ghoreishi and Haghighi, 2003). However, in present study this cannot be applied because reduction is speedier in environment without oxygen.

Chemical oxygen demand (COD) and total organic carbon (TOC)

Three best performing operational conditions from all treatment systems applied were selected for monitoring the decrease in COD and TOC level. A significant decrease in COD and TOC value was observed by these treatment systems (Figure 6) indicating the efficiency of applied redox reagents and making it clear that inside the media there are such chemical reactions taking place which are disrupting large xenobiotic recalcitrant molecule of dye (reactive black CNN) into simpler fragments.

FTIR analysis

To examine the decomposing mechanism of reactive black CNN further, FTIR analysis was performed using Shimadzu FTIR spectrophotometer. Figure 7 and 8 show the infrared spectrums of Reactive Black CNN before and
Figure 6. Effect of oxidation, reduction and sequential treatment on COD and TOC value of Reactive Black CNN before and after treatment.

Figure 7. Infrared spectrum of reactive black CNN.
Figure 8. Infrared spectrum of reactive black CNN after treatment with (a) KMnO$_4$ (b) Na$_2$SO$_3$ and H$_2$O$_2$ (c) Na$_2$SO$_3$ and Ferrioxalate.
after decolorization treatments, respectively. Comparing intensity and position of spectral peak confirm complete dissociation of –N=–N– group in treated samples. Appearance of –NO₂ peak in place confirm successful oxidation of azo group and its diminution leading to color removal. Moreover, the chance of formation of amines on treatment with a reducing agent remains there. Amines are supposed to cause toxicity to the environment, having carcinogenic potential (Fredrick et al., 1985). In this study, the amine formed as a result of reduction was further oxidized to nitro compounds. The oxidation of amine was reported in IR analysis as none of the amine bands were appeared in IR spectra.

Conclusions

Significant color removal of reactive black CNN was achieved by chemical oxidation and reduction processes in aqueous solution. From the present work following conclusions can be drawn: (1) KMnO₄ shows maximum color removal after 60 min in static mode; (2) Neither ferrioxalate nor H₂O₂ reacts significantly with dye when added individually; (3) Sequential treatment enhanced decolorization efficiency of H₂O₂ and ferrioxalate; (4) Highest color reduction of 97.64% was obtained by KMnO₄ in 100 ppm solution, 75.93% by combined treatment system of Na₂SO₃/ferrioxalate in 30 ppm solution and 62.19% by combined treatment system of Na₂SO₃/H₂O₂ in 40 ppm solution; (5) COD results showed 63.7 mg/L value in combined Na₂SO₃/ferrioxalate process while reduced TOC level of 72.8 mg/L was investigated again in Na₂SO₃/ferrioxalate treatment method; (6) Spectrums collected from FTIR analysis show degradation of azo group significantly and formation of nitro moiety was observed as an oxidative product of azo group.

Combined reduction-oxidation treatment method is a viable technique to decrease the color, COD and TOC amount effectively. The major benefit of this newly developed system is the key step of converting non-biodegradable dyes into degradable materials by reduction which suggests theoretical feasibility of the application of these processes.

REFERENCES


