Full Length Research Paper

Comparison of various oxidative treatments for removal of reactive black CNN

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Decolorization of reactive black CNN by chemical oxidation and reduction using $KMnO_4$, H_2O_2 and Ferrioxalate as oxidizing agents and Na_2SO_3 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 $KMnO_4$ and in alkaline medium with H_2O_2 and ferrioxalate. The most efficient methods for decolorization of reactive black CNN is oxidation using $KMnO_4$ as an oxidizing agent which removed 97.64% of dye. Maximum decolorization was obtained at 60 min of treatment under static conditions. H_2O_2 and ferrioxalate could remove only 50.71 and 44.21% dye, respectively. Sequential treatment was more successful with H_2O_2 and ferrioxalate when compared with $KMnO_4$. 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, $KMnO_4$, 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 (Stylidi et al., 2003). Largest industrial production of wastewater is related with textile industries involved in dyeing processes. An effluent resulting from dyeing cotton fabric and rinsing section 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 ($KMnO_4$, H_2O_2, and Ferrioxalate) and reducing agent (Na_2SO_3). Combined effect of reducing agent with each oxidizing agent was also analyzed for comparing efficiency of these method currently employed for the treatment of colored wastewater on large scale in

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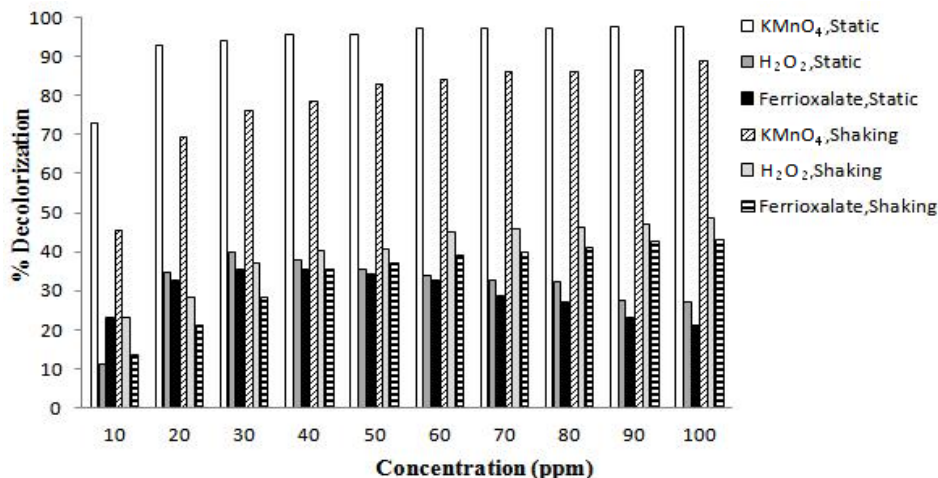
Figure 1. % decolorization of Reactive Black CNN at 60 min by various oxidation treatments.

European countries.

MATERIALS AND METHODS

Synthetic effluents of concentrations ranging from 10 to 100 ppm were prepared from stock dye solution for determination of λmax 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 H_2SO_4 acid and diluted NaOH base.

Individual treatment with reducing and oxidizing agents

The synthetic dye solutions were treated with $KMnO_4$, H_2O_2, ferrioxalate and Na_2SO_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 $KMnO_4$, 100 µl of 1 M hydroxylamine hydrochloride ($NH_2OH.HCl$) 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:

Decolorization efficiency (%) = {($A_{Initial}$ − A_{Final}) / $A_{Initial}$} × 100

$A_{Initial}$ = Absorbance before decolorization
A_{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 λ$_{max}$ 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 $KMnO_4$, 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 H_2O_2, 40% color removal was observed in solution having 30 ppm initial concentration. Efficiency decreased to 27% in 100 ppm solution on further increase
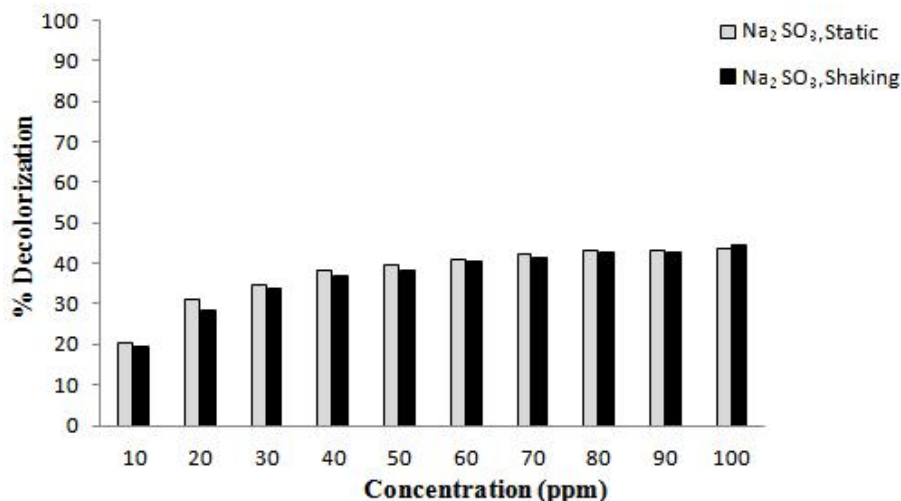
Figure 2. % decolorization of reactive black CNN at 60 min by reduction treatments.
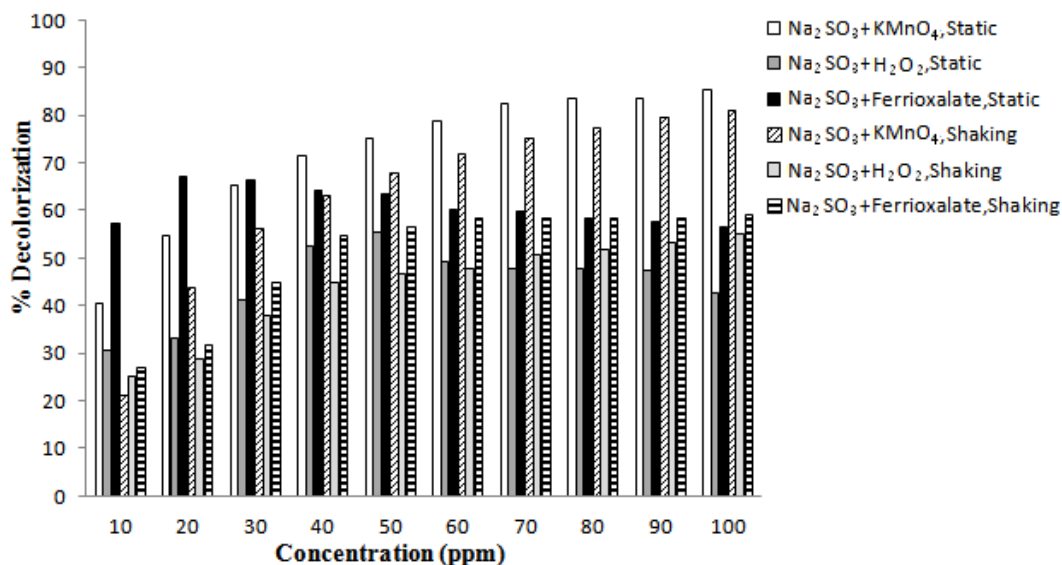

Figure 3. % decolorization of reactive black CNN at 60 min by sequential treatments.

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 H_2O_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 H_2O_2 alone as oxidizing agent, only 40% dye

removal could be achieved which is negligible to be used on large scale. Therefore, neither H_2O_2 nor ferrioxalate effectively reacts with dye when added individually (Salem et al., 2009).

Effect of reaction time

Better decolorization results were obtained with $KMnO_4$ at longer reaction time. However, in case of H_2O_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
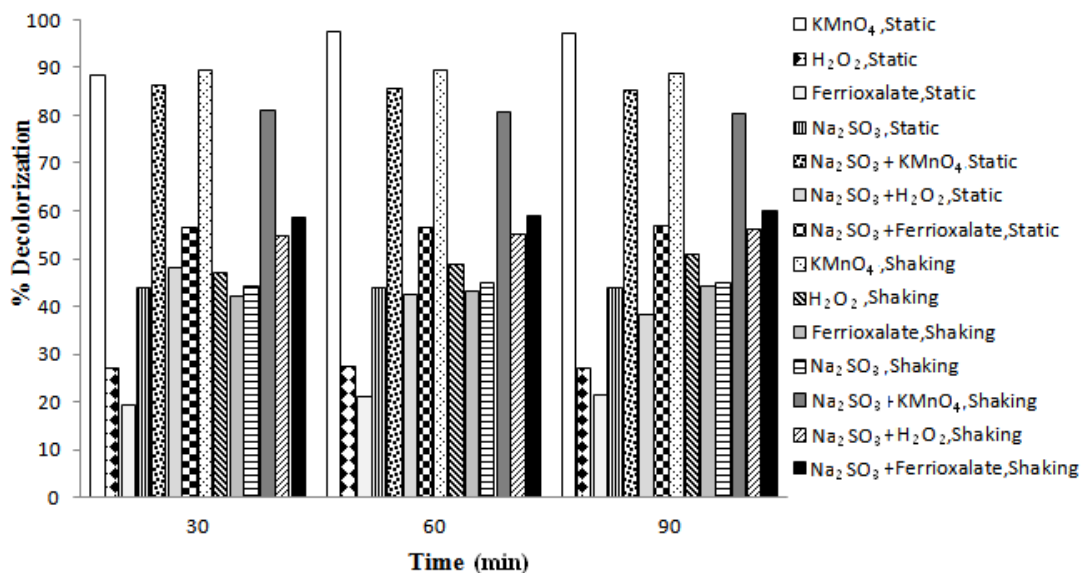
Figure 4. % decolorization of reactive black CNN solutions of 100 ppm at 30, 60 and 90 min by oxidation, reduction and sequential treatments.

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.
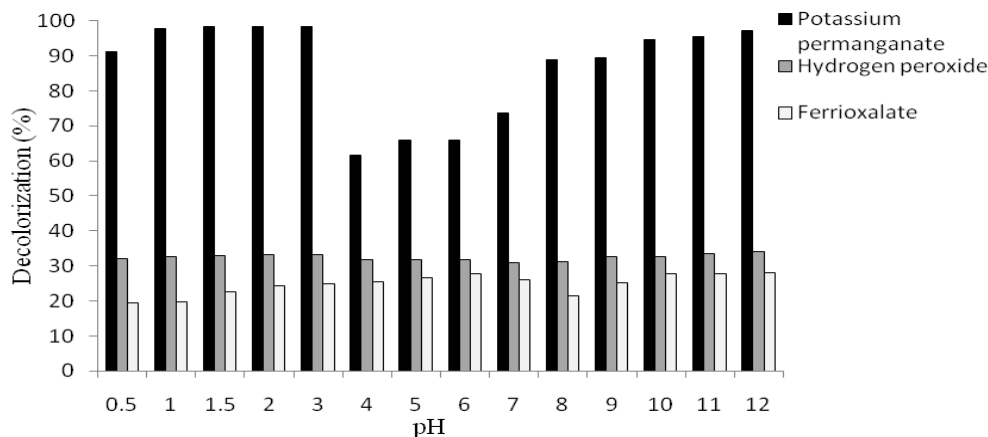
Effect of pH

On treatment with $KMnO_4$, 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 $KMnO_4$ (for dye decolorization) at acidic pH. Further experiments with $KMnO_4$ were performed at pH 1.5. Oxidation with H_2O_2 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 H_2O_2 was moving very slowly at pH less than two (Figure 5). It may be because of the increased stability of hydrogen peroxide 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 H_2O_2 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 $KMnO_4$, H_2O_2 and ferrioxalate was investigated individually both under static and shaking conditions. It was observed that $KMnO_4$ 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 $KMnO_4$ needed to remove all kind of azo dyes can vary in accordance with the sum of color causing

Figure 5. Effect of pH on % decolorization of Reactive Black CNN with various oxidizing agents.

functionalities present in dye structure and the influence of neighboring group on production of reaction intermediates.

Decolorization is achieved by H_2O_2 under static condition represented very little degradation ability. The decline in degradation is perhaps a result of free radical steeling activity of H_2O_2 (Fernandez et al., 1999). In experiment performed with shaking, H_2O_2 removed dye significantly up to 50.71% which indicated more pronounced color removal under shaking condition (Figure 1). Hydrogen peroxide undergoes self scavenging action when present in large quantity and generate hydroperoxyl radical (Dutta et al., 2002; Muruganandham and Swaminatham, 2004). This hydroperoxyl radical terminate the reaction by the formation of water and oxygen molecule when comes in contact with hydroxyl radical (Dutta et al., 2002). It can be concluded from the previous data that hydrogen peroxide is not a practicable oxidizing method when used individually (Ince and Gonenc, 1997; Liao et al., 2000; Shu et al., 1994; Yang et al., 1998) and evidence collected in this study supports this finding.

With ferrioxalate, the dye removal was less in static condition as compare to that on shaking. Maximum color removal of 44.21% was recorded in shaking experiments (Figure 1). A consistency was noticed in the results of ferrioxalate on shaking that the decolorization increased gradually with increase in concentration. However, the absorbance of synthetic wastewater lowers only a little on adding iron oxalate complex to it. This act is possibly because of some kind of complex formation within dye and ferrioxalate. This conclusion is in agreement with the one presented in literature (Park and Choim, 2003).

Effect of sequential treatment of reducing and oxidizing agents

Combination of H_2O_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 Na_2SO_3 was compatible with H_2O_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
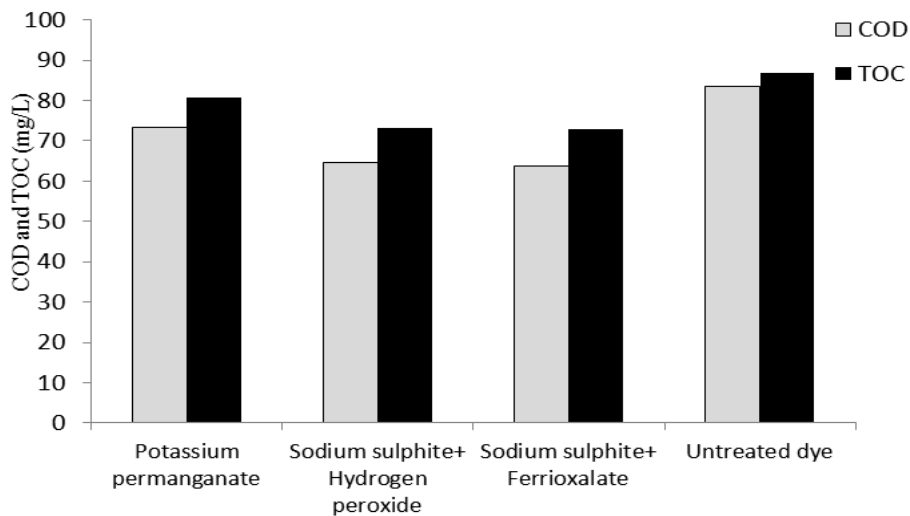
Figure 6. Effect of oxidation, reduction and sequential treatment on COD and TOC value of Reactive Black CNN before and after treatment.
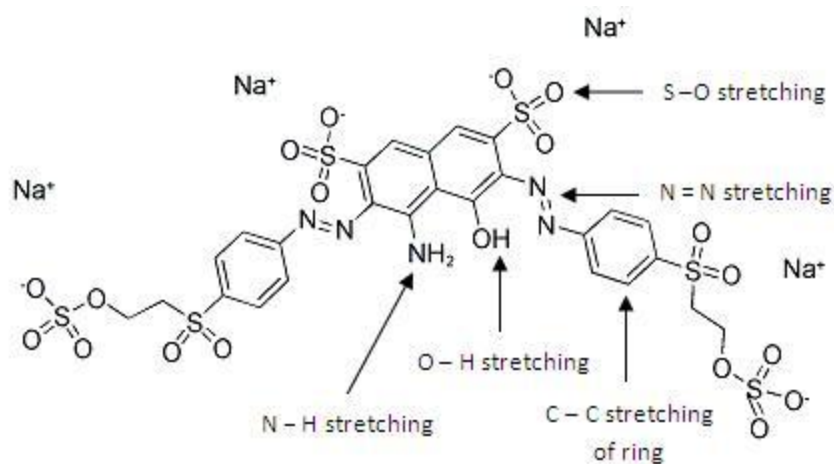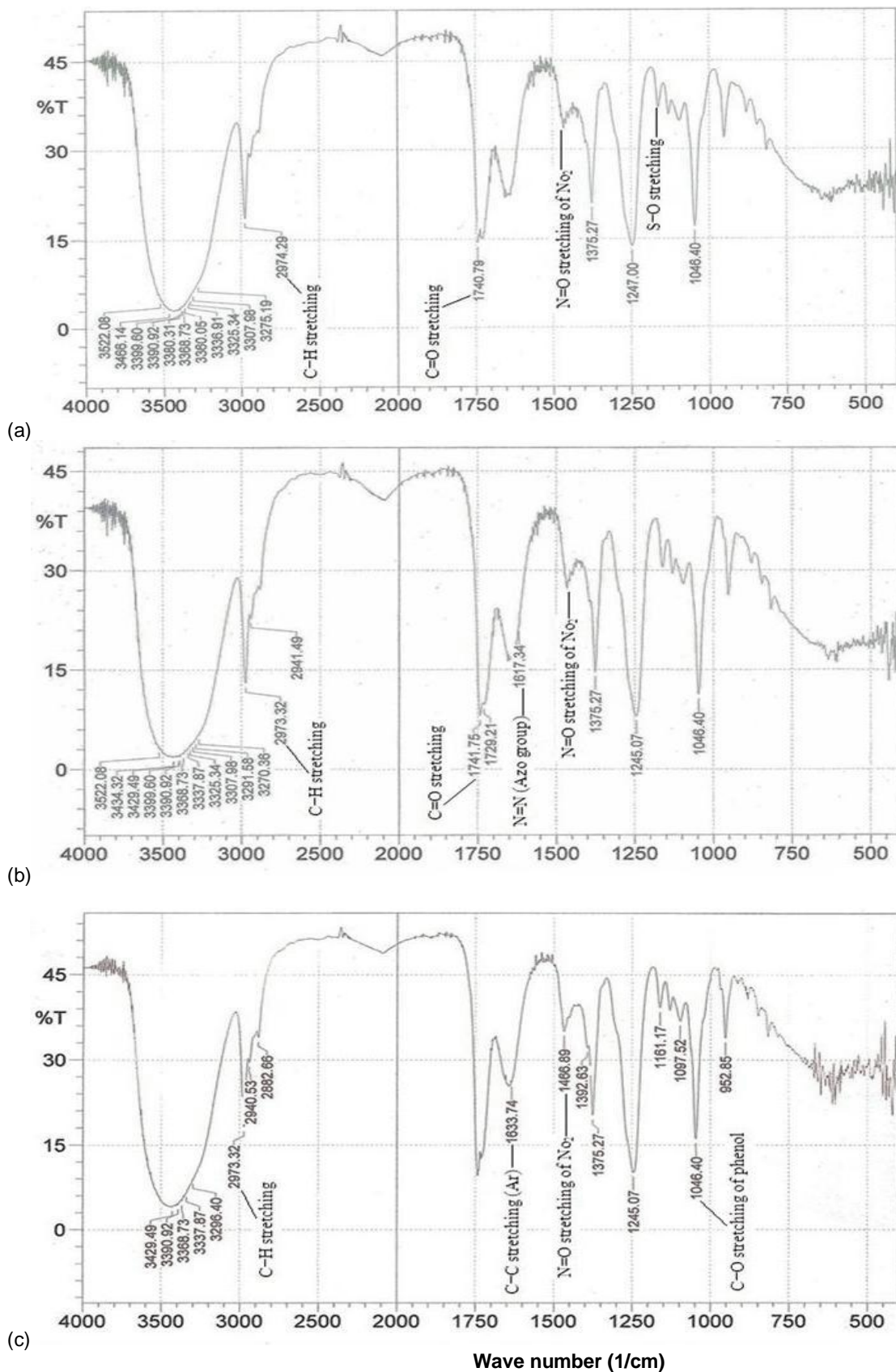

Structure of Ramazol Black B
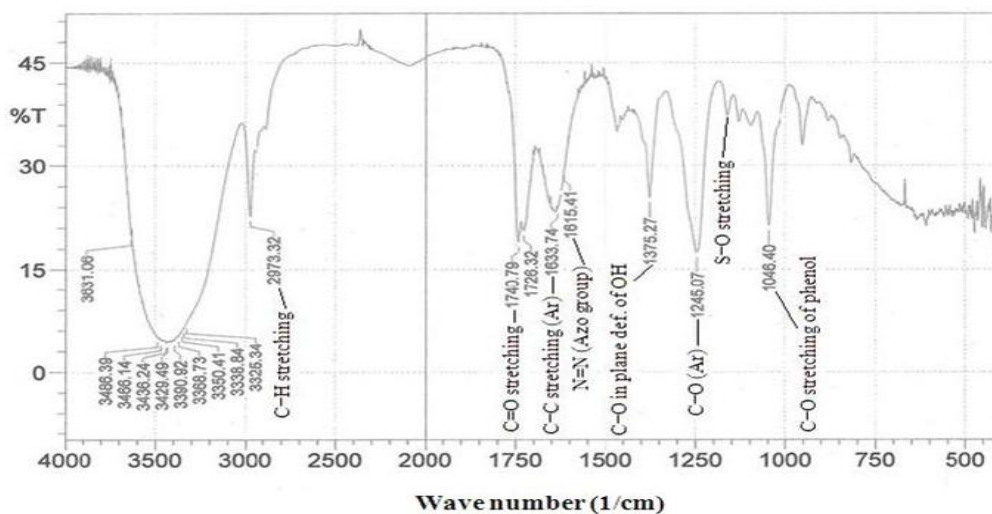
Figure 7. Infrared spectrum of reactive black CNN.

Figure 8. Infrared spectrum of reactive black CNN after treatment with (a) $KMnO_4$ (b) Na_2SO_3 and H_2O_2 (c) Na_2SO_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 –NO_2 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) $KMnO_4$ show maximum color removal after 60 min in static mode; (2) Neither ferrioxalate nor H_2O_2 reacts significantly with dye when added individually; (3) Sequential treatment enhanced decolorization efficiency of H_2O_2 and ferrioxalate; (4) Highest color reduction of 97.64% was obtained by $KMnO_4$ in 100 ppm solution, 75.93% by combined treatment system of Na_2SO_3/ferrioxalate in 30 ppm solution and 62.19% by combined treatment system of Na_2SO_3/H_2O_2 in 40 ppm solution; (5) COD results showed 63.7 mg/L value in combined Na_2SO_3/ferrioxalate process while reduced TOC level of 72.8 mg/L was investigated again in Na_2SO_3/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.

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