



## Optimization of Operational Parameters for Removal of Reactive Red 195 from Synthetic Wastewater by Sequential Redox Process

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The effectiveness of a combined reduction-oxidation treatment system for the removal of reactive red 195 (RR 195) from the synthetic wastewater was investigated. In this treatment system, sodium sulphite ( $\text{Na}_2\text{SO}_3$ ) was used as reducing agent and potassium permanganate ( $\text{KMnO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrioxalate [ $\text{Fe}(\text{OX})$ ] were employed as oxidizing agents. The influence of pH, concentration of reducing agent and oxidizing agents and initial concentration of dye was examined in the lab scale experimental studies. Spectroscopical results indicated that  $\text{H}_2\text{O}_2$  and ferrioxalate in combination with  $\text{Na}_2\text{SO}_3$  decolourized 63.61 and 71.28 % of reactive red 195, respectively, at optimized conditions while  $\text{KMnO}_4$  alone showed 99.34 % decolourization efficiency. The water quality was also monitored by chemical oxygen demand and total organic carbon. There was reduction in chemical oxygen demand and total organic carbon values, which indicated chemical decomposition of recalcitrant complex structure of dye. FT-IR analysis of products obtained after sequential treatment also confirmed the degradation during the process. Overall comparison revealed that potassium permanganate had excellent potential to decolourize reactive red 195.

**Key Words:** Oxidation, Reduction, Wastewater, Chemical oxygen demand, Total organic carbon, FTIR.

### INTRODUCTION

Due to large amount of water consumed in textile industry (especially in the process of dyeing), it has become the greatest generators of effluents. The effluent generated from these industries contains a wide range of dyes and other complex products. There is reduction in dissolved oxygen demand due to liberation of coloured wastewater into lakes and rivers thus making anoxic environments which are hazardous to inhabitant organisms<sup>1</sup>. Dyes present in the aquatic ecosystems reduce the penetration of light into deeper layers, which decline the quality of water, hinder the photosynthetic process and lower the solubility of gas that cause severe toxicity in aquatic life. Dye containing wastewater may also cause damages to the human body, kidneys, liver, reproductive system, brain and nervous system<sup>2-4</sup>. A number of methods have been employed to treat wastewaters such as adsorption<sup>5</sup>, coagulation<sup>6</sup> and membrane methods<sup>7</sup> that are useful physical and chemical processes for decolourization but these method utilize more chemicals and energy and may generate sludge<sup>8</sup>. Combination of two or more methods for the successful and complete removal are employed to meet the permissible discharge of

wastewater. Combined chemical coagulation and electrochemical<sup>9</sup>, combination of activated sludge, chemical coagulation and electrochemical oxidation process<sup>10</sup> and combined ion exchange, electrochemical method and chemical coagulation<sup>11</sup> have been used to treat coloured effluent. However, there is only limited research on the combined treatment process of reduction and oxidation to remove reactive dyes. The objectives of the present work were to optimize environmental conditions for efficient removal of dye by redox process.

### EXPERIMENTAL

The commercial dye reactive red 195 was provided by a local textile industry and was used as such without any further purification. Chemical structure of reactive red 195 is given in Fig. 1. Solutions of potassium oxalate and ammonium ferric sulfate were mixed with 3:1 molar ratio in order to prepare ferrioxalate complex ( $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot\text{H}_2\text{O}$ ) symbolized as  $\text{Fe}(\text{OX})$ <sup>12</sup>.

Experiments were run at various dye concentration (10-100 ppm) under shaking as well as static conditions. Efficiency of applied reducing agent as well as oxidizing agents was checked in ratios 1:1 and 1:2 at different time intervals 30,

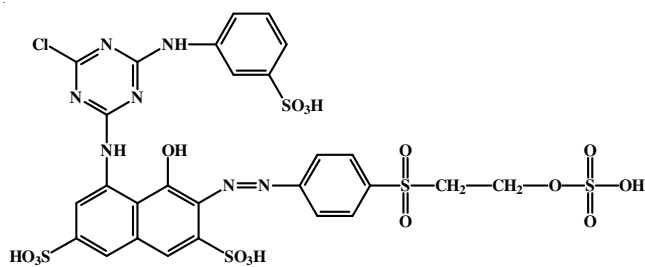


Fig. 1. Chemical structure of reactive red 195 (vinyl sulphone dye)

60 and 90 min separately as well as in sequential manner<sup>13,14</sup>. Standard methods of decolourization assay based on UV-VIS spectroscopy was used to get colour removal index. Decolourization was determined by measuring the absorbance of decolourization media at  $\lambda_{\max}$  542 nm and percentage decolourization was calculated as follows:

$$\text{Decolorization efficiency (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

where,  $A_0$  = absorbance of the dye solution (initial absorbance)  $A_t$  = absorbance of the treated dye solution at specific time,  $t$  (final absorbance).

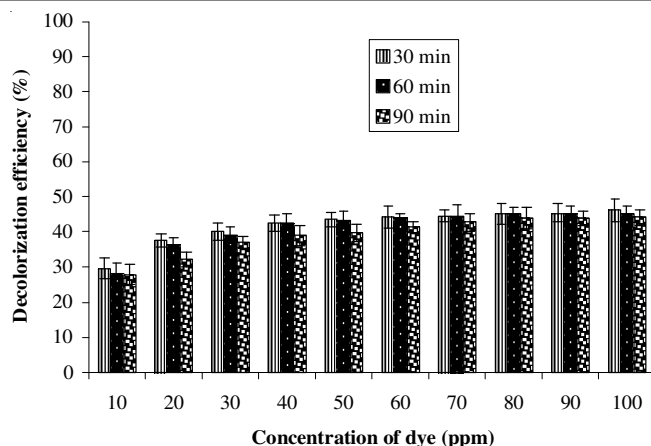
The quality of water after sequential treatment was determined by measuring the chemical oxygen demand (COD) and total organic carbon (TOC) following standard methods<sup>15</sup> with some modification. FT-IR spectroscopy was used for the prediction of possible products being formed during combined treatment of reactive red 195 with reducing and oxidizing agents. The extract of metabolites produced during treatment of reactive red 195 was prepared with ethyl acetate<sup>1</sup>.

## RESULTS AND DISCUSSION

### Treatment of reactive red 195 with reducing agent:

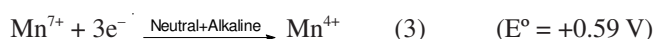
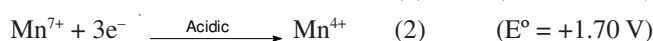
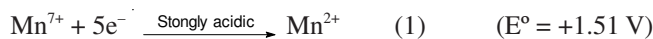
The effect of concentration of sodium sulphite on colour removal of reactive red 195 was evaluated at different time intervals under static conditions and by varying the concentration of dye solution from 10-100 ppm (1:1) as shown in Fig. 2. The decolourization efficiency was 29.6 % at 10 ppm and then increased by increasing the concentration of reducing agent upto 46 % at 100 ppm. Maximum colour removal was observed at time interval 0.5 h and by further increase in time there was slight decrease in colour removal. This might be due to reason that longer contact time between reducing agent and dye molecules, larger amount of secondary coloured aromatic amines had formed. These being coloured could not lead to higher colour removal. Decrease in colour removal at longer contact time has also been reported earlier<sup>16</sup>. There was no major difference in decolourization under shaking and static conditions by reducing agent. So, static conditions were chosen for the removal of reactive red 195 by  $\text{Na}_2\text{SO}_3$ .

An inefficient colour removal was noted by using reducing agent *i.e.* only 46 %. This lower efficiency can be attributed to fact that reducing agent caused reduction of azo bond ( $-\text{N}=\text{N}-$ ), which resulted in formation of aromatic amine, itself a recalcitrant molecule. It could not go under any further chemical change under reducing environment. So colour was not completely removed which was obvious from colour (greenish yellow) of media obtained after reduction treatment.

Fig. 2. Decolourization efficiency of reactive red 195 by  $\text{Na}_2\text{SO}_3$  under static condition with 1:1 ratio

### Treatment of reactive red 195 with oxidizing agents:

In order to find out the influence of pH on removal of RR 195 by applied oxidizing agents, pH was changed from 1-12 with HCl and NaOH at 90 min and 100 ppm concentration of dye solution as shown in Fig. 3. % decolourization of reactive red 195 by potassium permanganate was maximum *i.e.* 99.3 % at pH 1. It was decreased gradually by increasing pH upto 12 with colour removal value of 57.46 %.



Reactions indicated that  $E^\circ$  is higher in acidic solution as compared to alkaline solution. Thus, the mechanism depends on the substrate as well as the pH of medium during oxidative treatment. The results obtained in study presented here are in good agreement with earlier studies<sup>13,14</sup>.

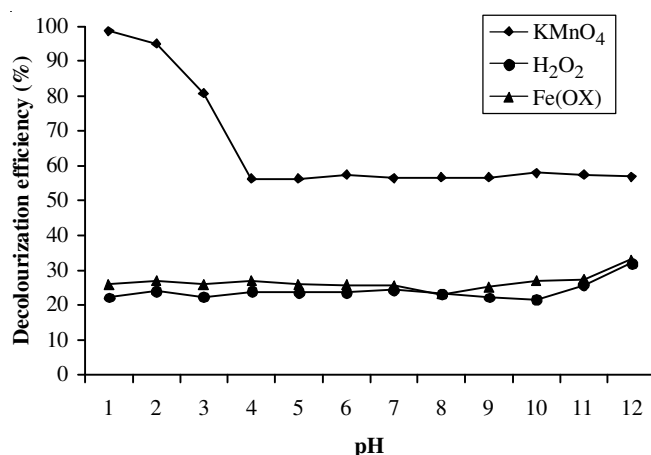


Fig. 3. Effect of pH on decolourization efficiency of reactive red 195 at 90 min under static conditions

Decolourization (%) of reactive red 195 by hydrogen peroxide was only 22 % in acidic conditions which negligibly increased with shift of pH from acidic to alkaline media. A shift of decolourization potential by pH has also been postulated by Lucas and Peres<sup>17</sup> who reported that increase in % decolourization in basic medium is due to the existence of large amount of  $\text{OH}^-$  ions which could help in the generation of hydroxyl

radicals, thus make the oxidation of dye easier. Similar trend with pH change on efficiency of hydrogen peroxide has also been reported<sup>18-20</sup>.

Colour removal of dye by potassium permanganate increased by increasing the dye concentration. Increase in colour removal efficiency of reactive red 195 might be due to the increase in the number of molecules of dye per unit volume, which increase the chance of collision between oxidizing agent and reactive red 195. Aleboye *et al.*<sup>13</sup> reported the similar results while studying the effect of concentration of dye on colour removal from synthetic wastewater. While in case of hydrogen peroxide and ferrioxalate colour removal was increased by increasing the concentration of dye upto 30 ppm and then decreased by further increase in dye concentration. The reason behind this enhance colour removal by increase in initial dye concentration is that amount of dye molecules increase with increase in concentration of reactive red 195 up to a certain limit and after this limit colour removal was decreased due to limited amount of oxidizing specie in a reaction mixture<sup>21,22</sup>. Effect of shaking on decolourization of potassium permanganate, hydrogen peroxide and ferrioxalate was evaluated by varying the dye concentration from 10-100 ppm (1:1 ratio of dye and oxidizing agents) at 90 min time intervals as shown in Fig. 4. Shaking decreased the colour removal efficiency of  $\text{KMnO}_4$  by 26 % as compared to static conditions because  $\text{KMnO}_4$  shows a negative effect on decolourization (%) under shaking conditions<sup>23,24</sup>. While in case of  $\text{H}_2\text{O}_2$  and  $\text{Fe}(\text{OX})$ , there was 10 % increase in

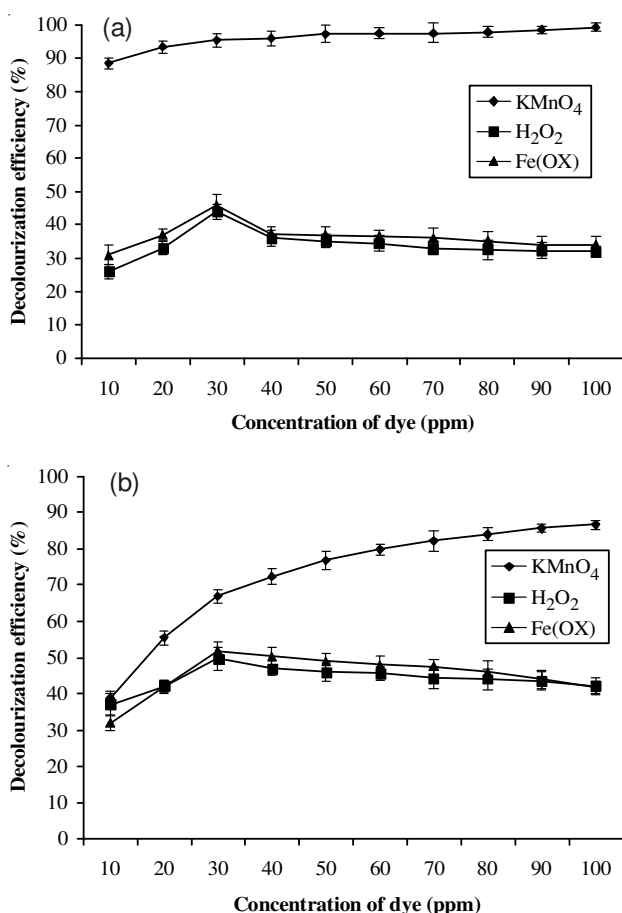


Fig. 4. Decolourization efficiency (%) of reactive red 195 at 90 min under static (a) and shaking (b) conditions

colour removal in shaking conditions when compared with static conditions. Because shaking increase the aeration, which help in oxidation ability of oxidizing specie. Higher colour removal at shaking environment might be also due to increased contact between  $\text{OH}$  radical and dye molecule.

**Combined sequential treatment:** By combining reduction and oxidation operations the overall dye removal efficiency was significantly increased. 69.6 and 71.28 % colour removal efficiency was observed by  $\text{H}_2\text{O}_2$  and  $\text{Fe}(\text{OX})$  when combined with  $\text{Na}_2\text{SO}_3$  in shaking conditions while  $\text{KMnO}_4$  alone give 99.3 % colour removal under static conditions. This is due to the greater oxidative ability of potassium permanganate and same higher oxidative capability was also reported<sup>13</sup>. Salem *et al.*<sup>12</sup> also reported that hydrogen peroxide and ferrioxalate alone not decolourized the dye significantly. Treatment of dye with sodium sulphite separately produced aromatic amines which itself a carcinogenic compounds. Therefore, sequential treatment ( $\text{Na}_2\text{SO}_3$  + oxidizing agents) of reactive red 195 is preferred to remove colour effectively and reduce toxicity produced by individual treatment process (Fig. 5).

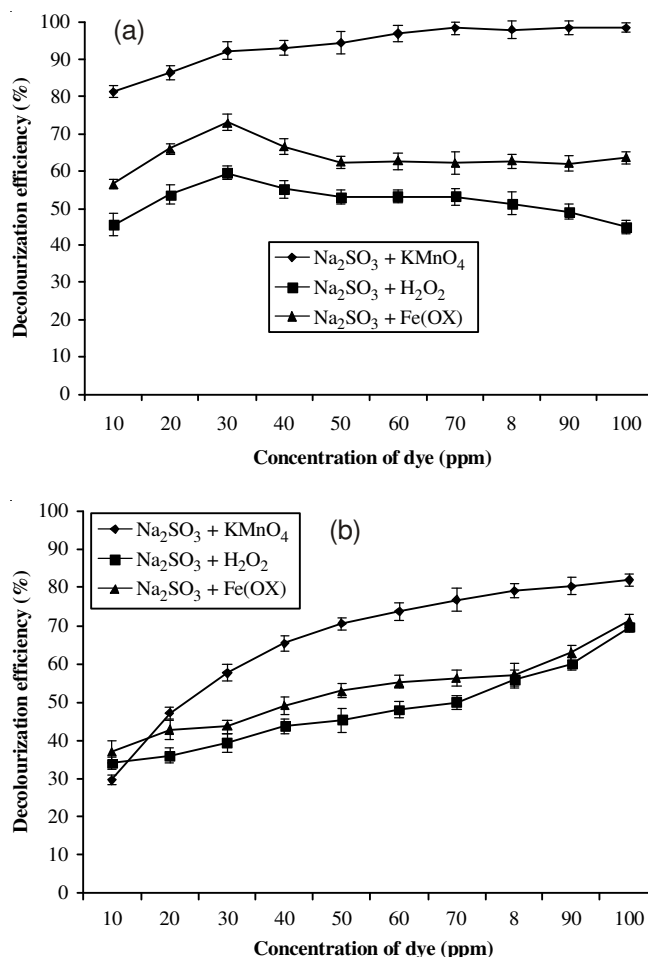


Fig. 5. Decolourization efficiency of reactive red 195 by sequential treatment at 90 min under static (a) and shaking (b) conditions

Mineralization of reactive red 195 by sequential treatment was also measured by chemical oxygen demand and total organic carbon. The chemical oxygen demand and total organic carbon values for untreated reactive red 195 were 75 and 45  $\text{mg L}^{-1}$ , respectively. 65, 67 and 69  $\text{mg L}^{-1}$  were the

chemical oxygen demand values where as 38, 39.66 and 40 mg L<sup>-1</sup> were the total organic carbon values for treated dye with potassium permanganate, hydrogen peroxide and ferrioxalate, respectively at best working condition. Values obtained indicating the small decrease in chemical oxygen demand and total organic carbon reduction values (Fig. 6) due to formation of new organic substances (xenobiotic) which are not coloured but require more time for degradation. Xu *et al.*<sup>25</sup> and Silva *et al.*<sup>26</sup> also reported that colour removal was greater than drop in chemical oxygen demand and total organic carbon values due to ease of destruction of chromophore.

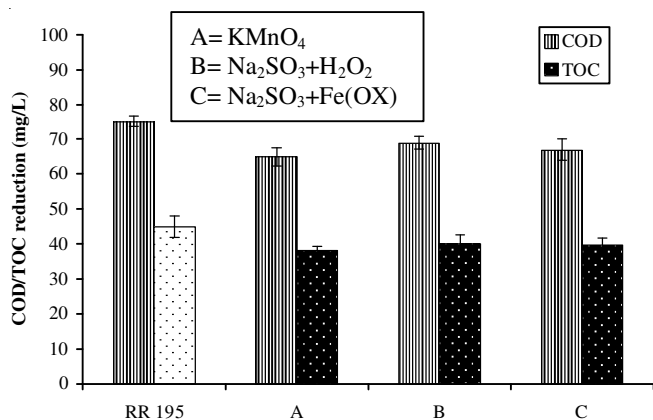


Fig. 6. Chemical oxygen demand and total organic carbon of reactive red 195 before and after sequential treatment at optimized conditions

**FT-IR characterization:** The FT-IR spectrum of untreated (control) parent dye reactive red 195 showed several bands in the 3500-3300 cm<sup>-1</sup> region indicated the existence of N-H and O-H moiety in dye structure. The band at 1615 cm<sup>-1</sup> in the untreated dye represented azo linkage (-N=N-). Presence of C-N bond was determined by two peaks, which appeared at 2942 cm<sup>-1</sup> and at 2882 cm<sup>-1</sup> due to symmetric and asymmetric vibrations, respectively. The band at 3422 cm<sup>-1</sup> described the presence of N-H moiety. Peak appeared at 1161 cm<sup>-1</sup> was due to stretching vibration of S=O. Due to C-Cl stretching vibrations band formed at 640 cm<sup>-1</sup>. The C-H stretching was represented by a band at 2974 cm<sup>-1</sup>. The bands of C-O stretching vibration at 1245 cm<sup>-1</sup> and 1046 cm<sup>-1</sup> specified the phenolic and alcoholic hydroxyl group, respectively. The band for aromatic ring appeared at 952 cm<sup>-1</sup> (Fig. 7). The FT-IR spectrum of sequentially treated reactive red 195 with reducing agent and oxidizing agents showed a considerable alteration in the positions of bands as compared to spectrum of untreated dye. Absence of

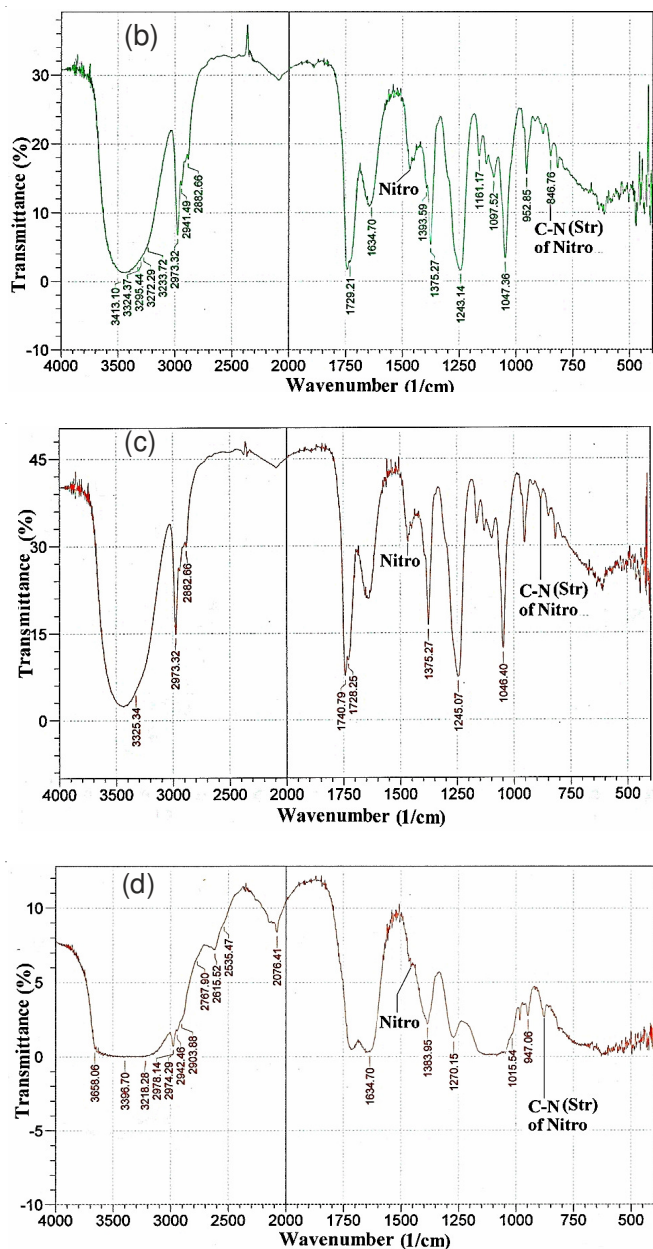
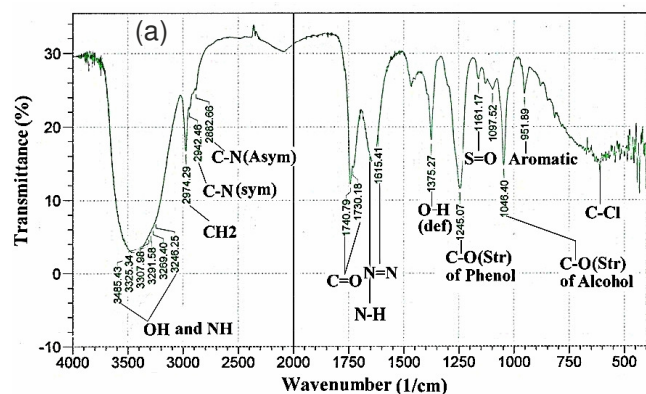


Fig. 7. FT-IR spectrum of reactive red 195 of untreated dye (a) and sequentially treated dye with KMnO<sub>4</sub> (b), Na<sub>2</sub>SO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (c), Na<sub>2</sub>SO<sub>3</sub> and Fe(OX) (d)

band at 1615 cm<sup>-1</sup> indicated the complete breakdown of azo bond. New bands were appeared at 1480 cm<sup>-1</sup> and 850 cm<sup>-1</sup> (C-N stretching) indicated the formation of nitro functionality moreover indication of C=O moiety confirm process of oxidation.

## Conclusion

The degradability of reactive red 195 under combined reducing and oxidizing conditions was studied to find maximum results. Experiments were carried out to examine the effect of different parameters (pH, concentration of dye, shaking and reaction time) on decolourization of reactive red 195. Results showed that pH greatly influence the decolourization efficiency. KMnO<sub>4</sub> showed maximum decolourization in acidic conditions while H<sub>2</sub>O<sub>2</sub> and Fe(OX) in alkaline medium. Shaking decreased the colour removal of KMnO<sub>4</sub> while increased the colour removal efficiency of H<sub>2</sub>O<sub>2</sub> and Fe(OX) by 10 % as compared

to static conditions. Combined treatment significantly increased the decolourization efficiency of H<sub>2</sub>O<sub>2</sub> and Fe(OX). Water quality parameters and FTIR analysis indicated the mineralization of reactive red 195. In fact, this method can be used as a pre treatment process for the mineralization of dye solution. It can be combined with the other methods to degrade wastewater completely.

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