Asian Journal of Chemistry

Vol. 22, No. 4 (2010), 3087-3093

# Applications of Advanced Oxidation Process for Industrial Wastewater Treatment

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Treatment of industrial wastewater using ultraviolet radiation in the presence of  $H_2O_2$  is an effective, innovative, promising and safe method. In the present study, advanced oxidation process has been employed for the treatment of wastewater of dyes industries. The samples were collected from 5 dyes manufacturing units located in industrial area, Faisalabad, Pakistan and their water quality parameters such as pH, colour intensity and chemical oxygen demand were analyzed. Three modes of treatments  $H_2O_2$ , UV and accumulative effect of  $H_2O_2$  and UV were employed on the wastewater. The results reveled that there was significant decrease of absorbance and COD after treatment. The removal of colour intensity and COD by UV treatment was significant while in case of  $H_2O_2$  treatment the COD reduction was up to 30 % while the colour removal was up to 70 % by the addition of 10 mM of  $H_2O_2$ . By combining both UV and  $H_2O_2$  treatments 95 % colour removal and 75 % COD reduction was achieved.

Key Words: Synthetic dyes wastewater, Advanced oxidation process, Colour intensity, Decolorization, Chemical oxygen demand, Ultraviolet, Absorbance.

## **INTRODUCTION**

With increasing industrialization and urbanization, water pollution has become a serious problem due to liquid effluents coming from different industries predominantly dyes and textile industries located in the premises of Faisalabad. Many industries, like textile, paper and plastics, tanneries, food, *etc.*, use dyes in order to color their products and consume substantial volumes of water, as a result generate a considerable amount of coloured wastewater<sup>1</sup>. Over 100,000 dyes are commercially available and the presence of very small amount of dyes in water even up to level of 1 ppm is highly visible and undesirable<sup>2</sup>. Due to good solubility, dyes are chief source of water pollution in industrial wastewater<sup>3</sup>. Wastewater coming from dyes

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industries is difficult to treat due to its resistance to aerobic digestion, stability to light, heat, oxidizing agents, *etc*. Keeping in view the chemical nature of dyes, it is necessary to eliminate dyes from wastewater before discharge into water bodies as most of the dyes are toxic, carcinogenic and hazardous to aquatic life<sup>4</sup>.

Only few dyes are biodegradable, the compounds, which are recalcitrant to biological treatment usually characterized as toxic and their removal from textile and dyestuff wastewater is a major concern<sup>5</sup>. The conventional treatment methods like coagulation, reverse osmosis, ultra filtration, adsorption etc., have been used for treatment of textile and dyes wastewater but all these methods are rather ineffective due to generation of sludge as well as high operating cost<sup>6</sup>. There is a dire need to establish method(s) to treat and eliminate pollutants from water and wastewater. Advanced oxidation process is an effective method for the degradation and mineralization of organic pollutants to eradicate the compound rather than transferring into solid phase. The  $UV/H_2O_2$  process has several advantages over others such as no sludge formation, operation at ambient temperature and formation of oxygen, which is helpful for aerobic decay process<sup>7</sup>. Furthermore, if the operation conceded out under suitable condition, the final products are H<sub>2</sub>O, CO<sub>2</sub> and low molecular weight aliphatic acids<sup>8</sup>. Among the advance oxidation process, chemical oxidation using UV in the presence of  $H_2O_2$  is a very promising technique by the generation of hydroxyl radicals. The hydroxyl radicals are short lived and highly reactive species that reacts non-selectively with organic matter present in wastewater, oxidize organic compounds and produce highly reactive radicals that facilitate further oxidation process. The possible reactions, which occur during UV/H<sub>2</sub>O<sub>2</sub> process, are hydrogen abstraction, electrophilic addition and electron transfer<sup>9</sup>.

During advanced oxidation process, degradation of aromatic structure, reduction in toxicity level, enhancement of biodegradation and elimination of dyes from wastewater are achieved<sup>10</sup>. The objective of present work is to investigate the photolysis of  $H_2O_2$  in presence of UV radiation for the generation of hydroxyl radicals during treatment for the discoloration as well as mineralization of dyes wastewater and its possible re-use for agricultural purpose. In the established literature little references are till available highlighting the UV/ $H_2O_2$  for the treatment of dyes wastewater.

### **EXPERIMENTAL**

The wastewater samples were collected directly from 5 local dye-manufacturing units located in the industrial area of Faisalabad city before going to mix with other stream and preserved in new pre washed PET bottles at 0 °C throughout the experiment.

Hydrogen peroxide was purchased from Fluka, Germany (35 % w/w), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, ferrous ammonium sulphate (FAS), NaOH and H<sub>2</sub>SO<sub>4</sub> were purchased from Merck, Germany. All the chemicals were of analytical grade, double distilled water was used for the preparation of solutions.

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**Treatment of samples:** The wastewater samples were treated by batch UV photo reactor emitting radiation having wavelength of 254 nm, 180 watt intensity, in presence and in the absence of  $H_2O_2$  for different time intervals 20-60 min. The combined effect of  $H_2O_2$  and UV also studied by adding different concentration (2 mM<sup>-10</sup> mM) of  $H_2O_2$  and UV irradiation time for the removal of colour substances as well as minimizing chemical oxygen demand (COD)<sup>5</sup>.

**Analyses:** The wastewater samples were analyzed spectrophotometerically in order to find their  $\lambda_{max}$  and absorbance by double beam UV-visible spectrophotometer (U-2001 Hitachi) using double distilled water as a blank. Chemical oxygen demand (COD) was determined by open reflux method using standard potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) and ferrous ammonium sulphate (FAS)<sup>11</sup>, while pH was determined by pH meter (Hanna HI 9813). All the experiments were performed using wastewater samples before and after treatment.

#### **RESULTS AND DISCUSSION**

The water samples were analyzed for pH, colour intensity and chemical oxygen demand (COD) before and after treatment with UV radiation,  $H_2O_2$  and UV/ $H_2O_2$ . The data showed that the absorbance values of the samples before treatment were 1.582 at  $\lambda_{max}$  472 (nm), 2.522 at  $\lambda_{max}$  530 (nm), 1.787 at  $\lambda_{max}$  394 (nm), 1.696 at  $\lambda_{max}$  492 (nm) and 1.298 at  $\lambda_{max}$  596 (nm), COD values were 790, 657, 895, 939 and 677 mg/ L while pH values were 9.7, 1.9, 1.7, 1.8 and 1.6 for samples 1, 2, 3, 4 and 5, respectively.

Effect of hydrogen peroxide concentration for colour removal: It was believed that an optimum amount of  $H_2O_2$  is required during reaction. The progressive OH<sup>•</sup> free radicals are produced till reaching equilibrium, after that further increase of concentration of hydrogen peroxide as well as time for ultraviolet radiation resulting into ineffective decolorization<sup>12</sup>.

During treatment with  $H_2O_2$ , 39-70 % colour amputation was noted by the addition of 2-10 mM  $H_2O_2$  as shown in Fig. 1, while 50-95 % reduction was achieved when samples were treated by  $H_2O_2$  and UV radiation for 0.5 h as shown in Fig. 2. It was revealed from the data that after reaching at equilibrium the addition of hydrogen peroxide as well as UV dose is ineffective for the colour removal which is consistent with the previous study<sup>13</sup> perform in order to treat the synthetic dyes solution which require high  $H_2O_2$  concentration.

Effect of  $H_2O_2$  for COD reduction: Like colour removal COD reduction was also affected by  $H_2O_2$  concentration, when applied alone as well as in combination with UV (UV/ $H_2O_2$ ). Chemical oxygen demand values of wastewater samples were 790, 657, 895, 939 and 677 mg/L for samples 1, 2, 3, 4 and 5, respectively, which showed that pollution load of wastewater was very high, however, after treatment decline of the COD values was up to 30 % with  $H_2O_2$  alone but on combination with UV (Fig. 3). The treatment seemed to be more effective and the reduction was 60, 70 and 75 % of COD by 20, 40 and 60 min of UV irradiation, respectively as shown by Figs. 4-6.

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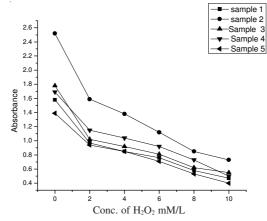


Fig. 1. Effect of H<sub>2</sub>O<sub>2</sub> on colour removal of dyes wastewater

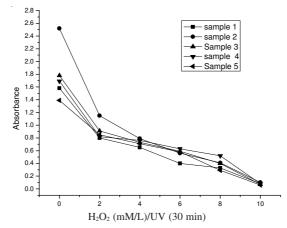


Fig. 2. Combined effect of  $H_2O_2$  and UV  $(H_2O_2/UV)$  on colour removal of dyes wastewater

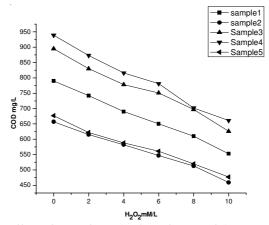


Fig. 3. Effect of  $H_2O_2$  for reduction of COD of dyes wastewater

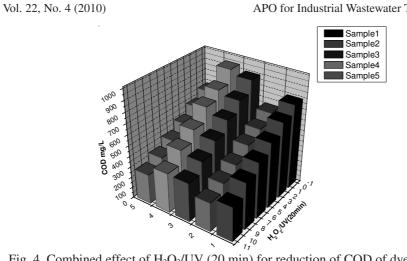


Fig. 4. Combined effect of H<sub>2</sub>O<sub>2</sub>/UV (20 min) for reduction of COD of dyes wastewater

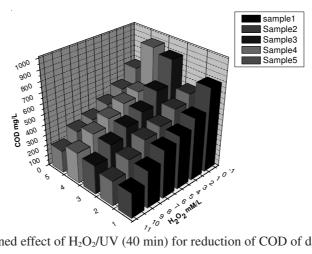


Fig. 5. Combined effect of H<sub>2</sub>O<sub>2</sub>/UV (40 min) for reduction of COD of dyes wastewater

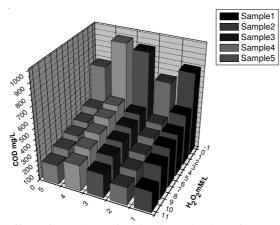


Fig. 6. Combined effect of H<sub>2</sub>O<sub>2</sub>/UV (60 min) for reduction of COD of dyes wastewater

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Chemical oxygen demand is an important water quality parameter that determines the amount of oxygen required by organic matter in a given liquid sample for its oxidation by strong chemical oxidant. The results revealed that effective COD disappearance was achieved in both the conditions because hydroxyl radicals destruct the organic molecules due to which COD values reduced.

**Effect of UV radiation:** The effect of UV radiation for the different time periods was evaluated by its decrease in colour intensity and COD reduction in wastewater. The reduction in colour intensities were up to 7, 12 and 20 % when treated for the period of 20, 40 and 60 min using 180W UV lamp as shown in the Fig. 7. The efficiency of the process was enhanced up to 95 % when both UV/H<sub>2</sub>O<sub>2</sub> treatment were employed as shown in Fig. 2. The reduction in COD *versus* irradiation time for UV is shown in Fig. 8 and the accumulative effect of UV/H<sub>2</sub>O<sub>2</sub> is shown in Figs. 4-6. The COD reduction was up to 75 % in UV/H<sub>2</sub>O<sub>2</sub> process, since UV radiation absorbed by H<sub>2</sub>O<sub>2</sub>, produced the OH<sup>•</sup> which is a powerful oxidizing agent to decolorize as well as mineralize the wastewater.

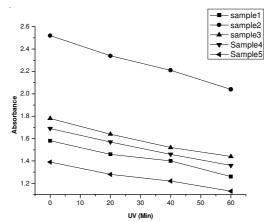


Fig. 7. Effect of UV radiation on colour removal of dyes wastewater

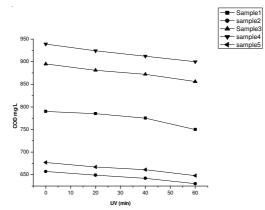


Fig. 8. Effect of UV radiation on reduction of COD of dyes wastewater

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## Conclusion

The UV/ $H_2O_2$  is an efficient process to treat the wastewater discharges from dyes and textiles industries. The intensity of UV radiation and optimum concentration of  $H_2O_2$  effectively reduce the colour intensity as well as COD, but the accumulative effect of UV and  $H_2O_2$  is more prominent. Advanced oxidation process is suggested a good option for industrial wastewater treatment because it is a safe, cheap, environmental friendly and non selective.

## ACKNOWLEDGEMENT

The authors are thankful to Mr. Muhammad Abbas, Director Harris Dyes and Pigment Industries, Faisalabad, Pakistan for his technical cooperation during sampling and experiments.

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(Received: 18 July 2009; Accepted: 31 December 2009) AJC-8243