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Oxidative Degradation of Reactive Violet 1 Dye by Ultraviolet Radiation in Presence of Hydrogen Peroxide

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Degradation of synthetic dye reactive violet 1 in aqueous media having concentrations 10-50 mg/L has been carried out by UV radiation in presence of H_2O_2. The change in colour intensity at λ_{max} 545 nm and chemical oxygen demand reduction was examined to evaluate the decrease in organic matter. The decrease in colour intensity was found 18, 25 and 100 % while chemical oxygen demand reduction up to 15, 25 and 55 % when solutions were treated by UV, H_2O_2 and UV/H_2O_2, respectively. The radiolytic end products were identified by FTIR and GC-MS, which revealed that advanced oxidation process had achieved the complete mineralization. The effect of different operational parameters such as initial dye concentration, UV irradiation time and concentration of hydrogen peroxide on degradation efficiency has also been evaluated. This treatment can be extended to dye containing industrial wastewater.

Keywords: Reactive violet, Radiolytic degradation, FTIR, GC-MS.

INTRODUCTION

It is generally observed that the effluents outcome from dyes manufacturing and textile processing industries is of intense colour due to ineffective treatment methods before being discharged. These effluents not only reduce transparency but also cause damage to the surface and underground water which impose adverse effects on human health. The abundantly complex feature of dye processing effluents contain high colour and chemical oxygen demand (COD) resulting into serious environmental issues[1-3]. Due to ineffectiveness of conventional treatment methods, there is need for an innovative method to treat the persistant pollutants such as synthetic dyes dissolves in aqueous media. Advanced oxidation process using UV light in presence of H_2O_2 is an effective treatment technology for the generation of powerful oxidant such as hydroxyl radical to treat the dyes as a model system as well as industrial effluents[4]. The advanced oxidation process using UV radiation and H_2O_2 which are characterized by the generation of hydroxyl radicals, the short lived and highly reactive chemical species that react non- selectively with organic substance in wastewater. The possible reactions which occur during UV/H_2O_2 process are hydrogen abstraction, electrophilic addition and electron transfer reactions. This technique has also several advantages over the other treatments such as no sludge formation, operative at ambient temperature, oxygen formed during process and the final products are CO_2, H_2O and low molecular weight aliphatic carboxylic acid[5,6].

In the established literature no study has been reported for reactive Violet 1 dye with the help of UV/H_2O_2. In the present study advanced oxidation process have been carried out for the treatment of Reactive Violet 1 dye having concentration 10-50 mg/L. The effect of UV radiation exposure time, H_2O_2 concentration and combined effect of UV and H_2O_2 have been evaluated, however the end products were also studied by FTIR and GC-MS.

EXPERIMENTAL

The reactive Violet 1 dye was provided by Haris dyes and Chemicals (Pvt.) limited, Faisalabad, Pakistan. The commercial dye powder was used without prior purification. The chemicals used during the experiment such as ethyl acetate, potassium dichromate, ferrous ammonium sulphate, hydrogen peroxide, sodium hydroxide and sulphuric acid were of analytical grade

(Merck, Germany). The triply distilled water was used for the preparation of different concentrations of dye 10-50 mg/L and other solutions used during study.

Treatment of samples: The aqueous solutions of dye were treated by batch UV photo reactor emitting radiation having wavelength of 254 nm and 180 watt intensity in the presence and absence of H_2O_2 for different time interval (20-60 min). The combined effect of H_2O_2 and UV was also studied by adding different concentrations (2-10 mM) of H_2O_2 and irradiating dye solutions for optimum time.

Analyses: The dyes samples were analyzed by using (U-2001 Hitachi) double beam UV-visible spectrophotometer before and after treatment in order to find their λ_{max} and then change in absorbance at this λ_{max}. Chemical oxygen demand (COD) was determined by open reflux method using standard potassium dichromate and ferrous ammonium sulphate and the pH was measured by pH meter (Hanna HI 9813).

GC-MS and FTIR analyses: Gas chromatography mass spectrometry (GC-MS) and Fourier transform infra red (FTIR) analyses were performed in order to identify the degraded end products. Prior to analyses, the irradiated samples were extracted with redistilled ethyl acetate. The organic phase was decanted followed by dehydration with $MgSO_4$ for 24 h. The samples concentrated by rotatory vacuum evaporator and stored for further analysis[7].

RESULTS AND DISCUSSION

Effect of UV radiation on absorbance and reduction of chemical oxygen demand: The aqueous solution of dye exhibited λ_{max} in the visible region of spectrum at the wavelength of 545 nm. The results shown in Figs. 1 and 2 illustrate the decrease in colour intensity was up to 10, 16 and 18 % while chemical oxygen demand reduction was up to 7, 11 and 15 %, when the aqueous solutions of dye having concentration (10 to 50 mg/L) were exposed to UV radiation for 20, 40 and 60 min, respectively. The results also indicate that the efficiency of dye degradation is less due to partial fragmentation. The attributed fact behind these findings is of quantitative nature that UV radiation has insufficient energy for the complete ionization and degradation of organic structure of dye which

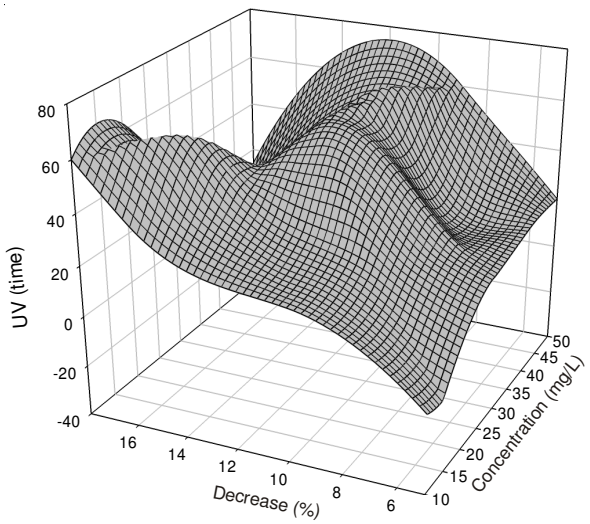

Fig. 1. Effect of UV radiation on absorbance of Reactive violet 1 dye

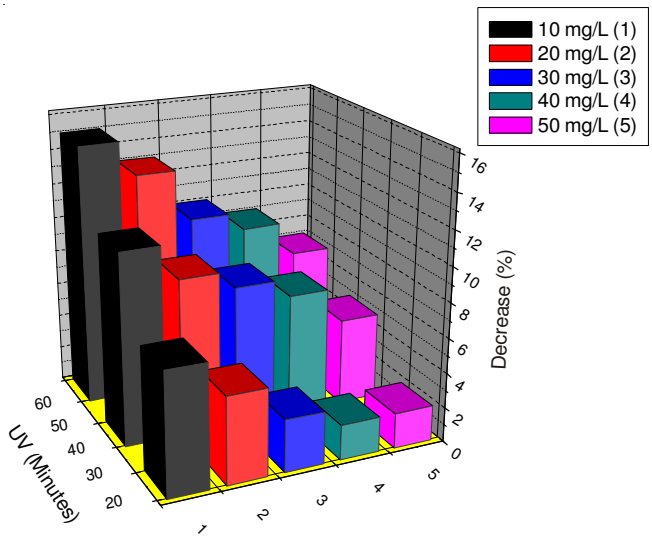

Fig. 2. Effect of UV radiation on chemical oxygen demand reduction of Reactive violet 1 dye

can not significantly reduce chemical oxygen demand values. It is also reported repeatedly that in most of the cases the treated dye solution regain the colour after UV treatment and this phenomenon was also observed in present study[8].

Effect of H_2O_2 on absorbance and reduction of chemical oxygen demand: The treatment of aqueous solutions of dye has been carried out by H_2O_2, which is a powerful oxidant used as colour bleaching agent. It is usual treatment of dye bath effluents to make it reusable[9,10]. The decrease in absorbance was observed to 23, 34, 44, 55 and 65 %, while chemical oxygen demand reduction was found to 9, 14, 17, 21 and 25 %, when 5-25 mM H_2O_2 was added in the dye solutions as shown in Figs. 3 and 4. The reduction in observed chemical oxygen demand was less as compared to colour removal of dye solutions since the colour removal occurred as chromophoric group disappeared while chemical oxygen demand reduction took place when the dye molecule split into low molecular weight carboxylic acid, carbon dioxide and water, *etc*.[8,11].

Effect of UV/H_2O_2 on absorbance and reduction of chemical oxygen demand: The synergistic effect of UV radiation and hydrogen peroxide has successfully utilized to degrade the pollutants present in the wastewater. The results show that decrease in colour intensity was up to 38, 67, 85, and 100 %, while the level of chemical oxygen demand was tested to

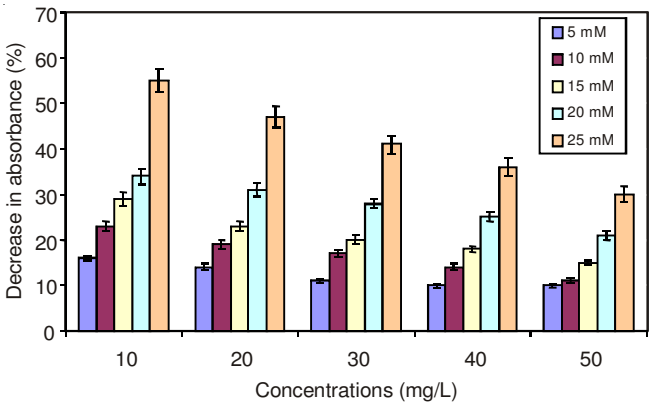

Fig. 3. Effect of H_2O_2 on absorbance of Reactive violet 1 dye

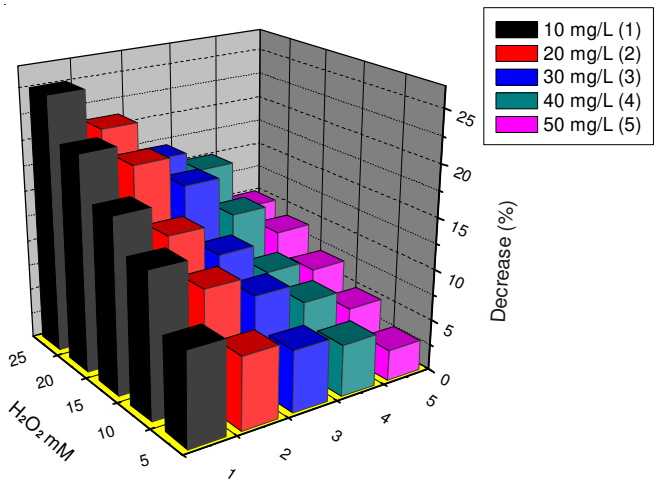

Fig. 4. Effect of H_2O_2 on chemical oxygen demand reduction of Reactive violet 1 dye

19, 30, 41, 48 and 55 % when the dye solution were treated with H_2O_2 having concentration 5-25 mM in combination with 60 min. UV exposure time (Figs. 5 and 6). It is reported that UV/H_2O_2 process effectively removes the chromophoric group of dye and subsequently extend this process until the complete mineralization of dye[12]. The UV radiation ($OH^•$) interacts with H_2O_2 resulting in the homolysis of H_2O_2 to form hydroxyl radicals which have oxidation potential of 2.8[10,11] react with pollutant non-selectively and degrade *via* oxidation reaction and ultimately convert into low molecular mass carboxylic acids, CO_2 and H_2O, *etc*. The treatment by UV/H_2O_2 is proficient for the reduction of colour intensity and chemical oxygen demand as a result of oxidative degradation of organic pollutants. It seems better than other advanced oxidation processes since it is rather simple, safe and green method[13-16].

Fourier transform infrared spectroscopic studies (FTIR) studies: The FTIR profile of untreated reactive violet 1 dye before treatment shows specific vibration peaks at 3480, 3430, 3030, 2366, 1575, 1545, 1403 and 1198 cm^{-1}, respectively which has already been discussed in our previous study[17].

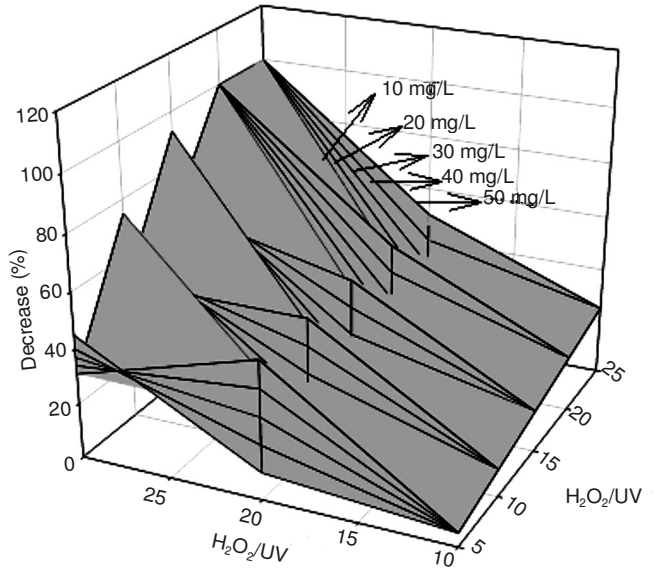

Fig. 5. Effect of UV/H_2O_2 on absorbance of Reactive violet 1 dye

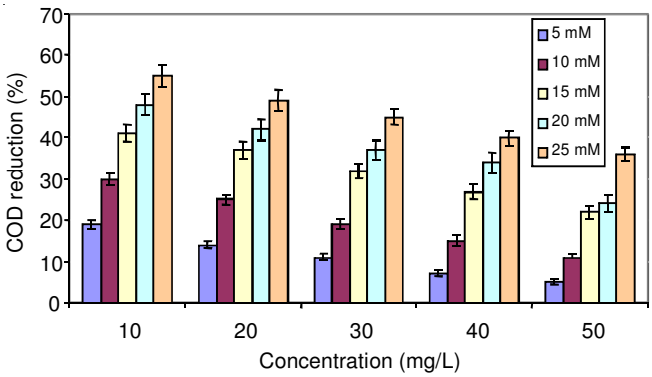

Fig. 6. Effect of UV/H_2O_2 on chemical oxygen demand reduction of Reactive violet 1 dye

The FTIR profile of treated dye (Fig. 7) clearly indicates that almost all characteristics peaks such as NH, OH, NH_2, N=N, C=C stretching as well NH, symmetric CH bending vibrations, disappeared in UV/H_2O_2 treated sample of dye having concentration 30 mg/L. There are some minor peaks appeared at 3400 and 1400 cm^{-1} that might be due to the stretching vibration of NH group and the bending vibrations of CH group respectively. It is evident from the FTIR studies that the destruction of aromatic ring occurred due to advanced oxidation treatment as well as mineralization of dye molecule.

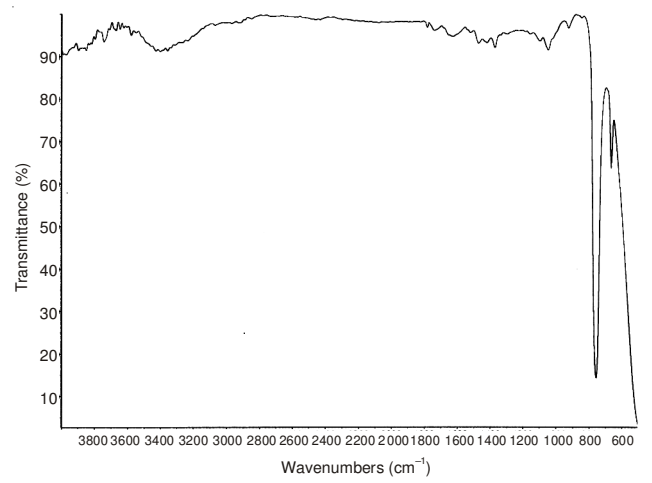

Fig. 7. FTIR profile of (30 mg/L) Reactive violet 1 dye treated with 25 mM H_2O_2 in presence of UV radiation

GC-MS studies: For the confirmation of spectroscopic studies (UV/visible and FTIR spectrophotometry) and chemical oxygen demand analyses, the treated samples were further analyzed by GC-MS. The profile of treated sample clearly indicates the complete breakdown of dye molecules into CO_2 and H_2O as well as the fragments of low molecular mass species. Mass spectrogram clearly indicate the removal of dye molecule after the treatment of UV/H_2O_2 support the assumption that advanced oxidation process is capable to degrade and mineralize the dyes leading to the formation of compounds having very low toxicity. The hydroxyl radicals generated during treatment practically attack on the dye molecule leading to its breakdown. The anticipated path way followed during reaction starts from the removal of azo groups present in the dyes,

formation of dye intermediates that may be of aromatic carboxylic acids which further fragmented into low molecular mass carboxylic acids and finally degraded into CO_2 and H_2O as a results of mineralization of dye[18].

Conclusion

The advanced oxidation process using UV in presence of hydrogen peroxide is an effective method to treat the dye as a model compound and furthermore the treatment can be extended to real dyes and textile effluents also. With the help of this process the dyes can be completely decolourize and the level of chemical oxygen demand reduction was up to 55 %. The degraded end products will be monitored by FTIR and GC-MS which revealed that the dye molecules have completely degraded and mineralize. The present methods is a good option to treat the industrial effluents.

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REFERENCES

1. E. Balanoskyand, F. Herrera, A. Lopez and J. Kiwi, *Water Res*., **34**, 582 (2000).
2. M. Vautier, C. Guillard and J.M. Herrmann, *J. Catal*., **201**, 46 (2001).
3. E. Rodriguez, R. Peche, J.M. Merino and L.M. Camarero, *Environ. Eng. Sci*., **24**, 363 (2007).
4. N. Daneshvar, M. Rabbani, N. Modirshahla and M.A. Behnajadya, *Radiat. Phys. Chem*., **B118**, 155 (2005).
5. M. Behnajady, A.N. Modirshahla and H. Fathi, *J. Hazard. Mater*., **B136**, 816 (2006).
6. M. Sanchez, H. Wolfger and N. Getoff, *Radiat. Phys. Chem*., **65**, 611 (2002).
7. A.S. Ozen, V. Aviyente and R.A. Klein, *J. Phys. Chem. A*, **107**, 4898 (2003).
8. H.Y. Shu and M.C. Chang, *Dyes Pigm*., **70**, 31 (2006).
9. A. Uygur and E. Kok, *J. Soc. Dyers Colour*., **115**, 350 (1999).
10. A. Uygur, *Color. Technol*., **117**, 111 (2001).
11. C.R. Huang and H.Y. Shu, *J. Hazard. Mater*., **41**, 47 (1995).
12. G.M. Colonna, T. Caronna and B. Marcandalli, *Dyes Pigments*, **41**, 211 (1999).
13. I.A. Alaton, I.A. Balcioglu and D.W. Bahnemann, *Water Res*., **36**, 1143 (2002).
14. S. Esplugas, J. Gimenez, S. Contreras, E. Pascual and M. Rodriguez, *Water Res*., **36**, 1034 (2002).
15. A. Aleboyeh, Y. Moussa and H. Aleboyeh, *Dyes Pigments*, **66**, 129 (2005).
16. E. Rodriguez, R. Peche, J.M. Merino and L.M. Camarero, *Environ. Eng. Sci*., **24**, 363 (2007).
17. M. Muneer, I.A. Bhatti, M. Iqbal and M. Ather, *J. Chem. Soc. Pak*., **34**, 787 (2012).
18. C. Hu, J.C. Yu, Z. Hao and P.K. Wong, *Appl. Catal. B*, **42**, 47 (2003).