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Photodegradation of Orange Green by Fe(III)–Aqua Complex

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Abstract

The photodegradation of orange green (OG) by excitation of Fe (III)-aqua complexes has been investigated under UV and solar light illumination. The rate of degradation has been found to be strongly influenced by the pH of the solution, initial concentration of Fe(III) and the nature of the light sources. The progress of removal of OG from solution has been monitored by recording the change of absorbance at λ_{max} = 480 nm, ($\epsilon = 1.27 \times 10^4$ L mol^{-1}cm^{-1} at 30°C), with time. The pH has been varied from 1.2 to 3.5. The initial concentration of Fe (III) was between 9.0×10^{-4} mol L^{-1} and 2.4×10^{-3} mol L^{-1}. The intensity of the UV artificial source was 14 Wm^{-2}, whereas the average intensity of the solar light during the experiments was about 700 Wm^{-2}. An optimistic result was obtained, when OG was irradiated by solar light. About 92% degradation of 1.5×10^{-4} mol L^{-1} OG solution has been done within 70 minutes by photodegradation using Fe(III)-aqua complex at pH 2.5 by UV light whereas about 86% degradation has been recorded by the solar light under the same conditions.

I. Introduction

Pollutants enter into soil and aquatic environment through the discharge of the industrial wastes and also through the decomposition of pesticides, herbicides, etc. The effluents of textile dying and knitting industries contain a large amount of unfixed azo dyes which come out into the environment without prior treatments. During the washing process, the exhausted reactive dyes are quite a large amount in their hydrolyzed and unfixed form[1,2]. Because of their non-biodegradability, toxicity and carcinogenic nature, these dyes constitute a major threat to the ecosystem[3] and cause a severe damage to the aquatic lives. Huge textile & dyeing industries at Narayonganj and Gazipur in Bangladesh are the main sources of textile wastewater that contains mainly dye effluents. These effluents of dyeing factories and some other industries constitute a dangerous problem to the aquatic environment near these cities.

A number of physical[4-7], chemical[8-10] and biological[11,12] methods are usually employed for the treatment of wastewater comes out from the textile dyeing and knitting factories. Among these methods, biological treatment seems to be cost-effective for some organic pollutants. However, it has been reported that most of the reactive dyes are not biodegradable because of their carcinogenic nature. Chemical methods such as chlorination and ozonation lead to complete oxidation of organics into carbon dioxide and minerals. But the discharging of chlorinated organic compounds, which are formed during the operation, into the environment causes more severe problems than caused by the effluents themselves. Ozonation is a much cleaner process but owing to instability of ozone, its on-site preparation is required. This involves significant capital costs. Physical methods such as adsorption, coagulation, ion-exchange, etc. have limited applicability owing to their high operational costs. Moreover, these methods only transfer the contaminants from one place to the other leaving the problem essentially unsolved. Therefore, attention has to be focused on the techniques that lead to complete destruction of the dye molecules into much cleaner materials.

Semiconducting oxide mediated photodegradation has drawn considerable attention over the last three decades in view of their potential applications in environmental related problems[13-15]. These oxides include mainly TiO_2 and ZnO, both of which have band gap energies of 3.0-3.2 eV corresponding to 410-380 nm wavelengths of radiation[16,17]. These materials are most widely used because of these being cost effective, photostable, and having high redox activity and selectivity. However, because of the large band gap energies of the oxide photocatalysts, these are particularly suitable for application under artificial UV irradiation that also involves considerable capital costs. Moreover, in large-scale applications, the use of suspended powder requires the separation and recycling of the ultrafine catalyst from the treated wastewater prior to the discharge, which is a time consuming and expensive process.

Recently, it has been reported that Fe(III)-aqua complexes photogenerate hydroxyl radicals, which can be used as photocatalysts[18-20]. It is interesting to note that unlike photo-Fenton process, no addition of hydrogen peroxide is needed in this system. Fe(III)-aqua complexes absorb a fraction of the available solar light up to 500 nm[21,22], while TiO_2 photocatalyst can use photon with wavelength close to 380 nm[23]. Therefore, Fe(III)-mediated photodegradation process can be expected as an efficient and inexpensive method for wastewater treatment and promotes the rate of degradation of various organic pollutants. The excitation of $[Fe(OH)(H_2O)_5]^{2+}$, the dominant monomeric species of aqueous ferric iron in acidic solution, is as follows[18-20]:

$$[Fe(OH)(H_2O)_5]^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} + 5\ H_2O \ldots\ldots\ldots \quad (1)$$

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$$Fe^{2+} + O_2\ (hv) \rightarrow Fe^{3+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Hydroxyl radicals are known to be reactive species involved in the advanced oxidation processes and, in most cases, to cause the complete mineralization of the pollutants. A number of papers have already been found in the literature, where hydroxyl radicals generated upon excitation of Fe(III)-aqua complexes have been used as photocatalysts to degrade organic pollutants[18-20,24-29]. The advantages of this photodegradation process are economical, rapid degradation and simple handling. Moreover, this ion is available in the natural environment. In this paper, we endeavor to use Fe(III)-aqua complex as a photocatalyst to degrade a typical textile dye, orange green (OG, Fig. 1) by using UV light as well as solar light.

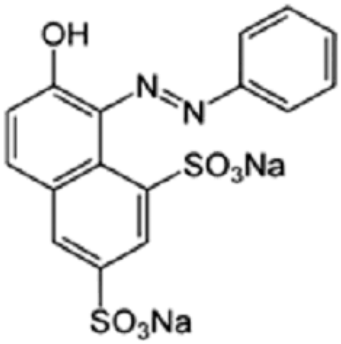

Fig. 1. Structure of orange green (OG)

II. Experimental

Commercial grade OG obtained from BDH, England was used here without further purification. All other chemicals were purchased from Merck, Germany. The double distilled water was used throughout the present study.

The photodegradation of the aqueous solution of dye was carried out in an open reactor of inside diameter 4.3 cm, height 5.5 cm. Light sources used were a UV lamp capable of emitting radiation of 254 nm and solar light. The reactor was placed on a magnetically stirred plate. The total system was enclosed in a wooden box called lamp house, inside surfaces of which were blackened (exception was for solar light). For solar light irradiation, the reactor was also placed on a magnetically stirred plate under natural environment. The time for the experiments was chosen between 11.00 am to 2.00 pm of sunny days in the month of April. The intensity of UV light was determined by using potassium ferrioxalate chemical actinometer[30]. The intensity of solar light was obtained from the Renewable Energy Centre of the University of Dhaka.

Homogeneous photodegradation was carried out in the reactor in the presence of Fe(III)-aqua complex under different light sources. Any water soluble ferric salt produces Fe(III)-aqua complex. A typical experiment was carried out by taking a definite concentration of dye in a fixed amount of ferric nitrate solution. It is well known that Fe(III) ions form precipitate at a pH higher than 3.5. Therefore, the photodegradation was carried out at different pHs to find out the optimum pH. Then the pH was adjusted to the optimum value by the addition of HNO_3 to prevent the precipitation of ferric ion for other subsequent experiments under different conditions.

III. Results and Discussion

The time courses of the UV absorption spectra of 1.5×10^{-4} mol L^{-1} solution in the photocatalytic degradation by Fe(III) aqueous ions has been observed in the range of 0-70 minutes (Fig. 2). The experimental conditions were $[Fe(III)]_o = 2.1 \times 10^{-3}$ mol L^{-1}, pH = 2.5 and UV light intensity = 14 Wm^{-2}. Fig. 2a was recorded with water as reference, whereas Fig. 2b was recorded with 2.1×10^{-3} mol L^{-1} $Fe(NO_3)_3$ solution as reference. Before illumination, the UV spectrum of OG solution with water as reference presents three absorption maxima at 480 nm, 328 nm and 242 nm, while that with $Fe(NO_3)_3$ solution as reference shows only former two peaks. The peak at 242 nm completely disappears due to the strong absorption by $Fe(NO_3)_3$ solution in this region.

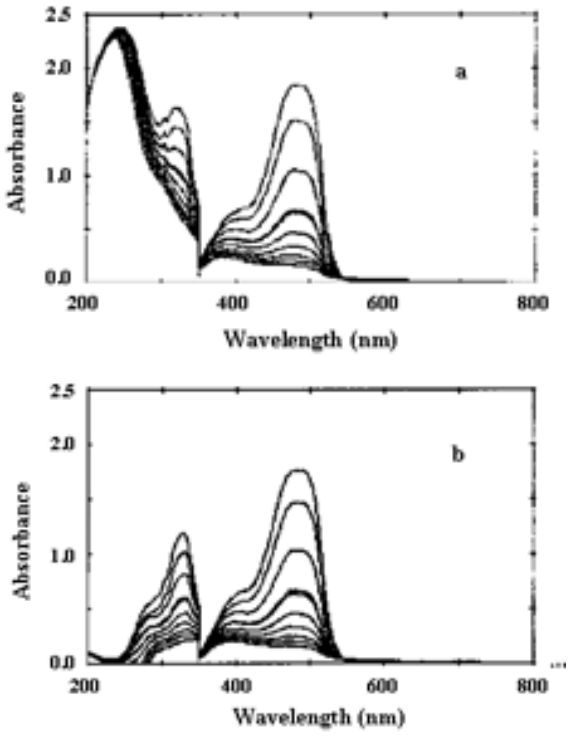

Fig. 2. UV-visible absorption spectra of 1.5×10^{-4} mol L^{-1} solution of OG during the photocatalytic degradation by Fe(III) aqueous ions at different times (from above for both figures): 0, 5, 10, 20, 30, 40, 50, 60 and 70 min. (a) with water as reference and (b) with 2.1×10^{-3} mol L^{-1} $Fe(NO_3)_3$ solution as reference.

The disappearance of both 480 nm and 328 nm absorption bands with increasing reaction time indicates that the dye molecules undergo decolourization as well as degradation. Consequently, it confirms that the monomeric Fe(III) aqueous ions, $[Fe(OH)(H_2O)_5]^{2+}$, is an effective photocatalyst for the degradation of OG under UV illumination.

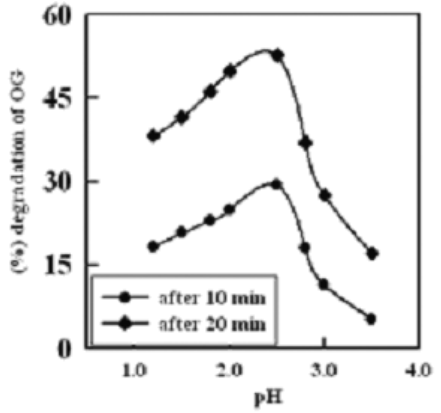

Fig. 3. Effect of pH on photodegradation of 1.5×10^{-4} mol L^{-1} solution of OG by Fe(III)-aqua complexes under UV irradiation. Initial concentration of Fe(III): 2.1×10^{-3} mol L^{-1}; light intensity: 14 Wm^{-2}.

Effect of pH on the photodegradation of OG in the presence of Fe(III)-aqua complex as a photocatalyst under UV irradiation has been investigated over the pH range between 1.2 and 3.5 because much precipitation of Fe (III) ions occur as $Fe(OH)_3$ above pH 3.5. These results are shown in Fig. 3. The percent degradation of OG increases with increasing pH up to 2.5. With a further increase in the pH, the percent degradation decreases rapidly. Katsumata et al[18] reported that the photodegradation of carbofuran by Fe(III)-aqua complex ($Fe_2(SO_4)_3$) showed a maximum at a pH = 2.8 due to production of the highest concentration of $[Fe(OH)(H_2O)_5]^{2+}$ species at this pH. Our observation is also in agreement with their results. It is likely that the concentration $[Fe(OH)(H_2O)_5]^{2+}$ ion, which is the active species, is lower at a pH lower than 2.5 because of the presence of excess H^+ ions. The concentration of this ion is also lower at a pH higher than 2.5 due to the precipitation of Fe(III) ion[18-22]. However, a small change in the degradation maximum may be related to the change of the metal salt from $Fe_2(SO_4)_3$ to $Fe(NO_3)_3$ or to the change of the substrate from carbofuran to OG. Since the degradation efficiency is maximum at pH = 2.5, all other subsequent experiments were carried out at this optimum pH.

Fig. 4 presents the effect of initial concentrations of Fe(III) ions on the photodegradation of OG. It has been found that the percent degradation OG can be greatly influenced by low concentrations of Fe(III) ions. With increasing the concentration of Fe(III) ions, the percent degradation increases. However, it shows almost a limiting value at ≥ 2.1×10^{-3} mol L^{-1} solution of Fe(III) ions. About 92% degradation of OG under these conditions was reached within 70 minutes. A bit longer time illumination will allow achieving complete degradation, while low concentration of Fe(III) did not allow achieving complete degradation in this process by the same time. According to Eq. 1, generation of $OH^{\bullet}$ radical needs light photon. Since, light intensity reaching at the reactor is constant for this particular source, the excess of Fe(III) ions remains practically ineffective after attaining a concentration of 2.1×10^{-3} mol L^{-1}.

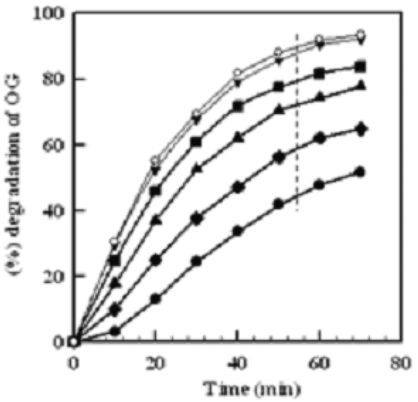

Fig. 4. Effect of initial concentration of Fe(III) ions on photodegradation of 1.5×10^{-4} mol L^{-1} solution of OG under UV irradiation. pH: 2.5; light intensity: 14 Wm^{-2}; Initial concentration of Fe(III) (from bottom along the dashed line): 0.9×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1}, 1.5×10^{-3} mol L^{-1}, 1.8×10^{-3} mol L^{-1}, 2.1×10^{-3} mol L^{-1} and 2.4×10^{-3} mol L^{-1}.

Fig. 5 shows a comparison of the degradation of OG in both dark and light environment. In the absence of Fe(III) ions, the degradation of OG is negligible even after 70 minutes of irradiation. On the other hand, in the presence of Fe(III) ions no decrease in the concentration of OG is recorded in the dark after 70 minutes. In the presence of 2.1×10^{-3} mol L^{-1} Fe(III) ions, the extent of degradation of OG has been evaluated for both UV light (intensity = 14 Wm^{-2}) and solar light with an average intensity of 700 Wm^{-2} in the month of April. Both UV light and solar light have been found to degrade the dye molecules. Since the photodegradation is mediated by $[Fe(OH)(H_2O)_5]^{2+}$ ions which absorb light of wavelength up to 500 nm, both of these lights are capable to produce $OH^{\bullet}$ radicals and cause dye degradation. However, a bit lower effectiveness of the solar light should be related to the fact that only a fraction of the light (<500 nm) is used up by the system for the purpose of photodegradation. Moreover, the light photons of solar light may be less effective in producing $OH^{\bullet}$ radicals compared to the UV light photons. These results imply that the photocatalytic reaction using Fe(III)-aqua complex is useful for the treatment of wastewater containing OG dye.

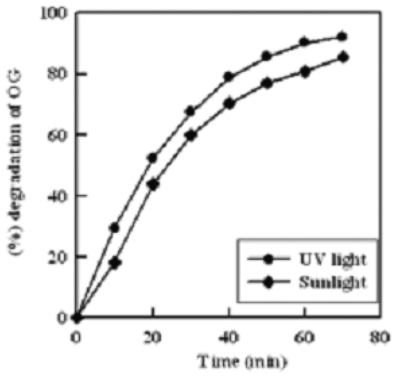

Fig. 5. Effect of light sources on photodegradation of 1.5×10^{-4} mol L^{-1} solution of OG by Fe(III)-aqua complexes. pH: 2.5, Initial concentration of Fe(III): 2.1×10^{-3} mol L^{-1}.

IV. Conclusions

Photodegradation of orange green (OG), a typical textile dye has been carried by Fe(III)-aqua complex under UV and solar light irradiation. The rate of degradation of OG by Fe(III)-aqua complex has been found to be affected by pH, concentration of Fe(III) ions and by the nature of the light sources. It has been found that the percent degradation is maximum at pH ≅ 2.5. With increasing the concentration of Fe(III), the initial rate increases and shows almost a limiting value at a concentration of ≥ 2.1×10^{-3} mol L^{-1}. Most interesting feature is that Fe(III)-aqua complex is an effective photocatalyst under both UV and solar light irradiation. Although some reports[3,4] showed better efficiency of degradation using Fenton's reagent than that of Fe(III)-aqua system, the latter system is environment friendly. This is because H_2O_2, which is a component of Fenton's reagent, is itself a pollutant causing dangerous problem to aquatic lives. On the other hand, Fe(III) ions is one of the most available ions in aquatic environment. Thus, this photocatalytic system could be useful technology for the treatment and the mineralization of organic compounds like azo-dyes even under solar light illumination.

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1. Pagga, U. and D. Brown, *Chemosphere* **15** (1986) 479.
2. Zolinger, H., *Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments,* VCH Publishers, New York, 1991.
3. Alaton, I.A., I.A. Balcioglu and D.W. Bahnemann, *Water Res.* **36** (2002) 1143.
4. Pollard, S.J.T., G.D. Fowler, C.J. Sollars and R. Perry, *Sci. Total Environ.* **116** (1992) 31.
5. Vandevivere, P. C., R. Bianchi and W. Verstaete, *J. Chem. Technol. Biotechnol.* **72** (1998) 289.
6. Reife A. and H. S. Freeman, *in: A. Reife, H. S. Freeman (Eds.), Environmental Chemistry of Dyes and Pigments*, Wiley, New York, 1996.
7. Allen, S.J., *in: G. McKay (Ed.), Use of Adsorbents for the Removal of Pollutants from Wastewaters*, CRC Press, Boca Raton, FL, 1996.
8. Alaton, I.A., A. Kornmuller and M. R. Jekel, *Color Technol.* **118** (2002) 185.
9. Masan, M. M. and C. J. Hawkyard, *Color Technol.* **118** (2003) 104.
10. Hademal, C., F. Boequillon, and O. Zahraa, *Dyes and Pigments* **49** (2001) 117.
11. Guoging, W., D. Henghi, C. Liu and Z. N. Liu, *Water Treat.* **5** (1990) 463.
12. Padmawathy, S., S. Sandhya and K. Swaminathan, *Chem. Biochem. Eng. Q* **17** (2003) 147.
13. Kumar, A. and N. Mathur, *Journal of Colloid Interface Sci.* **300** (2006) 244.
14. Leea, J.-M., M.-S. Kima, B. Hwangb, W. Baeb and B.-W. Kim, *Dyes and Pigments* **56** (2003) 59.
15. Mahmood, A. J., M. S. Islam and M. M. Hossain, *J. Bangladesh Chem. Soc.* **16** (2003) 36.
16. Poulios, I. and I. Aetopoulou, *Environ. Technol.* **20** (1999) 479.
17. Epling, G. A. and C. Lin, *Chemosphere* **46** (2002) 561.
18. Katsumata, H., K. Matsuba, S. Kaneco, T. Suzuki, K. Ohta and Y. Yobiko, *J. Photochem. Photobiol. A* **170** (2005) 239.
19. Brand, N., G. Mailhot and M. Bolte, *Environ. Sci. Technol.* **32** (1998) 2715.
20. Mailhot, G., M. Astruc and M. Bolte, *Appl. Organometal. Chem.* **13** (1998) 53.
21. Faust, B.C. and J. Hoign, *Atmos. Environ.* **24A** (1990) 79.
22. Benkelberg, H. J. and P. Warneck, *J. Phys. Chem.* **99** (1995) 5214.
23. Hoffmann, M. R., S. T. Martin, W. Choi and D.W. Bahnemann, *Chem. Rev.* **95** (1995) 69.
24. Bajt, O., G. Mailhot and M. Bolte, *Appl. Catal., B: Environ.* **33** (2001) 239.
25. Mailhot, G., M. Sarakha, B. Lavedrine, J. C´aceres and S. Malato, *Chemosphere* **49** (2002) 525.
26. Catastini, C., M. Sarakha, G. Mailhot and M. Bolte, *Sci. Total Environ.* **298** (2002) 219.
27. Poulain, L., G. Mailhot, P.W. Wah-Chung and M. Bolte, *J. Photochem. Photobiol., A: Chem.* **159** (2003) 81.
28. Catastini, C., S. Rafqah, G. Mailhot and M. Sarakha, *J. Photochem. Photobiol., A: Chem.* **162** (2004) 97.
29. Andrezzi, R. and R. Marotta, *Water Res.* **38** (2004) 1225.
30. Calvert, J. G. and J. N. Pitts, Jr. Photochemistry, John Wiley & Sons Inc. New York, 1990.