Heterogeneous Photo-Fenton Degradation of an Azo Dye in Aqueous H_2O_2/Iron Oxide Dispersions at Neutral pHs

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The photodegradation of Mordant Yellow 10 (MY10), a kind of azo dye, in aqueous dispersions of H_2O_2/hematite (α-Fe_2O_3), goethite (α-FeOOH) and akaganeite (β-FeOOH) at neutral pHs under UV-light irradiation was examined. The fastest degradation rate of MY10 was obtained with goethite. The formation of •OH in the photoreaction process was detected by ESR spin-trapping technique. A possible mechanism of heterogeneous photo-Fenton reaction was proposed.

Much attention has been directed at investigating the degradation of organic pollutants mediated by photo-Fenton reaction in the recent years.[1,2] It provides a possible and effective approach toward the degradation or mineralization of a wide variety of harmful/toxic pollutants in wastewaters. However, the photo-Fenton degradation of organic pollutants using Fe^{3+} or Fe^{2+} has many disadvantages which hold back the extensive application of this method to water treatment: first, the reaction must proceed at $pH < 4$. Second, the Fe^{3+} or Fe^{2+} ions adding to the reaction system have to be removed from the treated water after the photoreaction. Recently Kiwi and coworkers have explored heterogeneous photoassisted Fenton reactions on supported iron clusters to avoide the drawbacks of homogeneous treatment.[3,4] In this study, we report the photodegradation of an azo dye, Mordant Yellow 10 (MY10), in the presence of H_2O_2/iron oxides (α-Fe_2O_3, α-FeOOH, β-FeOOH) at neutral pHs under UV-light irradiation. A fast degradation rate of MY10 was observed with goethite. This work provides a promising way in the treatment of organic pollutants, particularly nonbiodegradable azo dyes at neutral pHs. In addition, since iron oxides and H_2O_2 are ubiquitous in environment water, soil and particles in air,[5,6] the research may also shed some light on the role of iron oxides in the natural environment.

The iron oxides were prepared according to previously published procedures.[7–10] High purity α-Fe_2O_3 was prepared as follows: 10 g $FeCl_3 \bullet 6H_2O$ was heated in a stove at 120 °C for one day. Then the pretreated $FeCl_3$ was dissolved in 500 ml doubly distilled water. The solution was adjusted to pH 14 with NaOH and was held at 95 °C for 3 days. After repeated washings with doubly distilled water by centrifugation and decantation, the formed hematite was stored in polythene bottles. α-FeOOH was prepared by an otherwise identical method to that for α-Fe_2O_3 except that the solution was aged at 70 °C at pH 12. β-FeOOH was prepared in a manner similar to that for α-FeOOH except that the solution was kept for 2 months. The structures of the iron oxides powder were verified by X-ray diffraction using a General Electric Model XRD-6 with $CuK_{\alpha 1}$ line radiation (ASTM no. 33-0664 for α-Fe_2O_3, no. 29-0713 for α-FeOOH and no. 34-1266 for β-FeOOH). The TEM (Philip Technai 20) pictures of the iron oxides showed that the goethite exhibited needle shape units with average size of 60 nm long and 9 nm diameter, the rod like hematite with average size of 50 nm long and 20 nm diameter and pearl like akaganeite with mean radius of 100 nm.

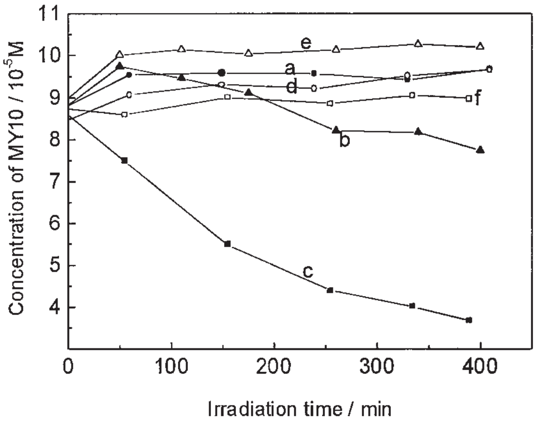

Figure 1. Concentration change of MY10 ($C_0 = 1 \times 10^{-4}$ M) under different conditions, initial pH = 8, $H_2O_2 = 1 \times 10^{-3}$ M, iron oxide = 0.5 g l^{-1}. a, b and c denote hematite, akaganeite and goethite, respectively, in H_2O_2/iron oxide dispersion; d, e, f corresponding to a, b, c but without H_2O_2.

Figure 1 shows the degradation of MY10 in the presence of different kinds of iron oxides at pH = 8. Irradiation experiments were carried out with a 100 W Hg lamp ($\lambda > 330$ nm, Toshiba Lighting and Technology of Japan) under continuously magnetically stirring. In typical experiments, a solution of 50 ml containing 1×10^{-4} M MY10, 1×10^{-3} M H_2O_2 and 0.5 g l^{-1} iron oxide was contained in a Pyrex glass vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for ca.30 min to establish the adsorption/desorption equilibrium between the dye and the iron oxide particle. At given irradiation time intervals, 5 ml dispersion were sampled, centrifuged, and subsequently filtered through a Millipore filter to remove iron oxide particles. The filtrates were analyzed by UV-Visible spectroscopy using a Lambda Bio 20 (Perkin Elmer) spectrophotometer. It can be found that the decomposition rate of MY10 can be significantly accelerated in the presence of goethite/H_2O_2 (curve c) comparing to the other two kinds of iron oxide (curve a, b) and the reaction systems without hydrogen peroxide (curve d, e, f). The degradation of MY10 in α-FeOOH/H_2O_2 dispersion proceeded via an apparent first order kinetic and 75% MY10 was decomposed after 400 min of irradiation. However, a little increase in the concentration of MY10 was found in curves a, b, d and e, which may be the result of the photodesorption of MY10 from the iron oxide particles. The change of total organic carbon (TOC) of MY10 (2×10^{-5} M) was also monitored in α-FeOOH ($0.5\,\mathrm{g\,l^{-1}}$)/H_2O_2 (2×10^{-3} M) dispersion under UV-light irradiation at pH8. The TOC decreased from 4.0 to 0.1 after 6 h of irradiation. The result showed that MY10 could be mineralized in excess H_2O_2 in the presence of goethite. Three control experiments (dark reaction of MY10/α-FeOOH/H_2O_2 and UV irradiation of MY10 and H_2O_2/MY10 solution) were also performed simultaneously. It was found that UV light irradiation resulted in no concentration change of MY10 in MY10 solution and only a small degree of degradation (ca. 18% and 22%, respectively) occurred in dark reaction and MY10/H_2O_2 solution under irradiation. It can be concluded that like the homogeneous photo-Fenton reaction, UV light can accelerate significantly the degradation of MY10, and H_2O_2 is a prerequisite in the reaction system. Therefore, the simple photocatalytic mechanism, in which the organic was oxidized by the photogenerated hole in the valence band of the semiconductor, is not applicable in this study. The total dissolved iron was determined spetrophotometrically by the *o*-phenanthroline method during the reaction process. Photodissolution of iron oxide[11] was not significant in the reaction since the highest concentration of total iron was lower than 20 μM. Furthermore, the concentration of the total dissolved iron increased little during the reaction process and the amount of iron dissolved from goethite was almost the same as the other two kinds of iron oxides.

On the basis of the experimental observations, we suggest a possible reaction mechanism of the heterogeneous photo-Fenton reaction on the degradation of MY10 under UV-light irradiation as follows:

$$\equiv Fe^{III}OH + H_2O_2 \rightarrow \equiv Fe^{III}OOH + H_2O \quad (1)$$

$$\equiv Fe^{III}OOH + h\nu \rightarrow \equiv Fe^{IV}{=}O + \bullet OH \quad (2)$$

$$\equiv Fe^{IV}{=}O + H_2O \rightarrow \equiv Fe^{III}OH + \bullet OH \quad (3)$$

$$\mathrm{MY10} + \bullet OH \rightarrow \text{degraded or mineralized products} \quad (4)$$

The reactions are initiated by the formation of a precursor surface complex of H_2O_2 with the oxide surface metal centers.[12] The similar surface complex was also observed in the H_2O_2/TiO_2 system.[13] Different from the iron ion in solution, the surface Fe is immobilized in the crystal lattice and octahedrally coordinated by O^{2-} and OH^-. So the activity of surface Fe may similar to that of coordinated iron compound other than the hydrolytic iron species in solution. Under UV irradiation, the excited $Fe^{III}O$-OH bond is broken to produce a $Fe^{IV} = O$ species and HO• radical.[14] The $Fe^{IV} = O$ is highly unstable and reacts immediately with H_2O forming another active hydroxyl radical. The •OH radicals attack the MY10 adsorbed on the surface of α-FeOOH, leading to its degradation and mineralization.

According to the photocatalytic degradation mechanism, •OH plays an important role in the photocatalytic reaction. Since the lifetime of •OH is very short, it cannot be detected directly. The spin-trapping EPR technique has proven to be useful in detecting radical species.[15,16] Figure 2 illustrates the 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) spin-trapping EPR spectra under different conditions. The irradiation source was a Quanta-Ray Nd:YAG pulsed laser system; $\lambda = 355$ nm, 10 Hz. There were no free radicals detected in the dark reaction (b) and MY10/α-FeOOH dispersion under irradiation for 1 min (a), while the characteristic four peaks from DMPO-•OH adducts with an intensity ratio of 1 : 2 : 2 : 1 appeared in the MY10/α-FeOOH/H_2O_2 system under UV irradiation (c). These results supply a proof for the proposed mechanism that the surface complex of H_2O_2 with the oxide surface decomposed under UV irradiation and produced •OH, which can oxidize the organic substances owing to their high oxidation potential ($E^0 = +2.80$ V).

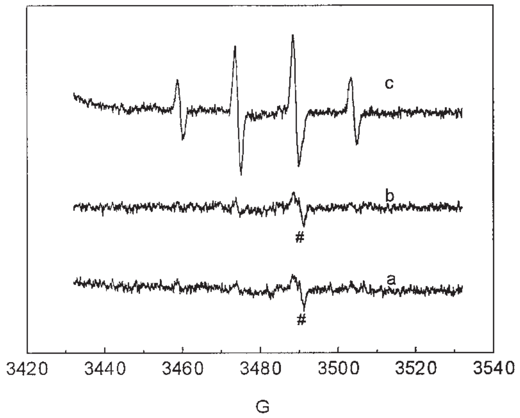

Figure 2. ERP signals of DMPO-•OH at 1 min of reaction. a: in MY10/α-FeOOH dispersion under UV irradiation; b: in MY10/H_2O_2/α-FeOOH dispersion in the dark; c: in MY10/H_2O_2/α-FeOOH dispersion under UV irradiation. #: The signal is caused by the disturbance of the quartz capillary tube.

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