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Photo Fenton degradation of high concentration Orange II (2 mM) using catalysts containing Fe: A comparative study

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ABSTRACT

Photo Fenton discoloration and mineralization of high concentration Orange II (2 mM) was conducted by using three catalysts containing Fe in the presence of 2 × 8 W UVC light (254 nm) and 100 mM H_2O_2 at an initial solution pH of 3.0. The three catalysts are laponite clay based Fe nanocomposite (Fe-Lap-RD), betonite clay based Fe nanocomposite (Fe-B), and iron oxide hydrated (FeOOH). All of them showed a good photo catalytic activity in the discoloration of 2 mM Orange II. 100% discoloration was achieved within 120 min in the presence of 1.0 g Fe-Lap-RD/L while 100% discoloration needs 180 min reaction in the presence of 1.0 g Fe-B or FeOOH. In terms of discoloration, the efficiency of the catalysts follows the order: Fe-Lap-RD > Fe-B ≈ FeOOH. However, in the mineralization of 2 mM Orange II, only Fe-Lap-RD and Fe-B showed good photo catalytic activity while FeOOH showed poor photo catalytic activity after 300 min reaction. In the cases of 1.0 g Fe-Lap-RD/L and Fe-B, more than 95–98% TOC removal of 2 mM Orange II can be achieved while only 82% TOC removal was obtained in the presence of 1.0 g FeOOH/L. In terms of the final TOC removal, the efficiency of the three catalysts follows the order: Fe-Lap-RD > Fe-B > FeOOH. The efficiency of 1.0 g Fe-Lap-RD/L is similar to that of 10 mg Fe^{3+}/L. The results revealed that using Fe-Lap-RD as a heterogeneous catalyst for the degradation of high concentration Orange II is successful. Furthermore, our results also illustrate that both homogeneous and heterogeneous photo Fenton reactions are responsible for the complete discoloration and mineralization of high concentration Orange II.

1. Introduction

Recently, heterogeneous photo Fenton reactions have received much attention in the photo degradation of organic dyes owing to their unique advantages of complete mineralization of organic pollutant, easy separation of the catalysts from the treated wastewater, and not causing secondary metal ion pollution. Many heterogeneous photo catalysts containing Fe ions, Fe cluster, and iron oxide have been developed for the reactions [1–14]. For example, Nafion film and pellet containing sulfonic groups that can effectively anchor Fe ions have been used to prepare heterogeneous catalyst for photo Fenton degradation of Orange II and Indigo Carmine [1–4]. He et al. studied heterogeneous photo Fenton degradation of an azo dye Mordant Yellow 10 in aqueous H_2O_2/iron oxide dispersions at neutral pHs [5]. In addition, Feng et al. synthesized laponite and bentonite clay based Fe nanocomposites (Fe-Lap-RD and Fe-B) and employed them as heterogeneous photo Fenton catalysts for the degradation of Orange II in the presence of UV light and H_2O_2 [6–9].

However, it should be pointed out that in those studies, the concentration of organic dyes in water is quite low. For example, in most studies on photo Fenton degradation of Orange II, the Orange II concentration is only 0.2 mM, which is much lower than real dye wastewaters [1–2,6–9]. There are at least two reasons for choosing such low concentration. One is that dye molecule itself can absorb UV light significantly so that when the dye concentration increases, the UV light for the photo Fenton reaction decreases, then, resulting in a decreased efficiency. Another is that as the dye concentration increases, the UV light penetration significantly decreases, then, also leading to a decreased efficiency [8]. However, if the dyes can be decolorized quickly and the intermediates formed do not absorb UV significantly, the amount of UV light for the photo Fenton reaction can increase rapidly. In this case, what will happen and can heterogeneous photo Fenton catalysts be used for the treatment of dye wastewater with a high concentration? There is no doubt that to address this issue has not only academic significance but also industrial application.

The objective of this paper is to explore whether the heterogeneous photo Fenton catalysts containing Fe can be used for the photo degradation of high concentration Orange II in the presence of UV light and H_2O_2. Three catalysts (Fe-Lap-RD, Fe-B, and FeOOH) were used for the photo Fenton degradation of 2 mM Orange II. Both

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discoloration and mineralization of 2 mM Orange II as a function of time were measured. The Fe leaching from the catalysts during reactions were studied. The contributions from both heterogeneous and homogeneous photo Fenton reactions were also discussed.

2. Experimental

2.1. Chemicals

The layered laponite and bentonite clays were supplied by Fernz Specialty Chemicals and Integrated Mineral Technology, Australia, respectively. Reagent grade $Fe(NO_3)_3{\cdot}9H_2O$, Na_2CO_3, and 30% H_2O_2 were obtained from Aldrich. Azo dye Orange II (certified) was purchased from Acros Organics, USA.

2.2. Preparation and characterization of the catalysts containing Fe

The preparation of laponite and bentonite clay based Fe nanocomposites (Fe-Lap-RD and Fe-B) have been described in detail in our previously published results [6,8]. In addition, FeOOH catalyst was supplied from Aldrich as received. All the three catalysts have also been fully characterized in our published studies [6,9].

2.3. Photo Fenton degradation of 2 mM Orange II

Photo Fenton degradation of 2 mM Orange II by using different heterogeneous catalysts was performed in a batch photo reactor as described previously [8]. The total volume of Orange II solution was 0.5 L. The Orange II and H_2O_2 concentrations used were fixed at 2 mM and 100 mM, respectively. The Orange II concentration is 10 times higher than those in many previous studies [1–2,6–9]. The choice of 100 mM H_2O_2 is owing to the fact that this concentration is the best for the degradation of 2 mM Orange II according to our previous studies [6,8]. The catalyst loading was fixed at 1.0 g/L, which is the best catalyst loading determined in our previous studies [6,8]. Two 8 W UVC lamps (Philips) (254 nm) were inserted in the center of the photo reactor as the UV light source. The reaction temperature was controlled to be 30 °C by a digital circulating water bath. An electromagnetic stirrer was used to ensure a good dispersion of the catalysts in solution. The initial solution pH is controlled to be 3.0, which is the optimal solution pH for both heterogeneous and homogeneous photo Fenton reaction [2]. The initial solution pH was carefully adjusted by the diluted H_2SO_4 solution, and measured by a pH meter (Thermo Orion: Model 420). In case of the degradation of 2 mM Orange II by using the heterogeneous catalysts above, the first 30 min is for the dark adsorption of Orange II on the surface of the catalysts. After 30 min dark adsorption, the 2 × 8 W UVC lamps were turned on, and 30% H_2O_2 was added to the Orange II solution.

2.4. Chemical analysis

It is known that Orange II shows the maximum absorption peak at 486 nm [2], the Orange II concentration in solution can be determined by measuring the absorbance of Orange II at 486 nm using a UV–vis spectrophotometer (Shimadzu Model UV Mini 1240) [6]. Before the measurement, a calibration curve was made by using the standard Orange II solutions with the known concentrations. A linear relationship between the absorbance of the standard solutions at 486 nm and Orange II molar concentration was obtained up to 0.1 mM Orange II. Because the reaction in the sample taken from the photo reactor continued after sampling, the measurement of absorbance of reaction solution at 486 nm should be finished within 1 min.

In order to obtain the total organic carbon (TOC) as a function of time with a good accuracy, 2.5 mL sample for TOC measurement was immediately treated with 2.5 mL scavenging reagent (0.02 M Na_2SO_3, 0.02 M KH_2PO_4, 0.02 M KI, and 0.01 M NaOH). Then, the TOC of the reaction solution was measured with a Shimadzu 500 instrument equipped with an auto-sampler (TOC 5000A).

In addition, to investigate the Fe leaching behaviors from the different catalysts during discoloration and mineralization of 2 mM Orange II, the Fe concentration in solution as a function of time was measured by induced coupled plasma (ICP) (Perkin–Elmer Model Optima 3000 XL). To avoid sampling mineral phase iron, the reaction solution was treated with a membrane filter with a pore size of 0.2 μm. Before the measurement, a high purity Fe standard solution (1000 ± 3.0 mg/L in 2% HNO_3) was diluted in 2% HNO_3 for making a calibration curve.

3. Results and discussion

3.1. Discoloration of 2 mM Orange II

Fig. 1 shows the discoloration of 2 mM Orange II under different conditions. Without any catalyst but only with 100 mM H_2O_2 and 2 × 8 W UVC (curve a), the discoloration is slow. After 300 min reaction, complete color removal cannot be achieved, indicating that H_2O_2/UVC system is not efficient in the treatment of high concentration Orange II in water. Without UV light and H_2O_2 but only with 1.0 g Fe-Lap-RD/L in the solution in the dark (curve b), the apparent discoloration of 2 mM Orange II is quite fast in the first 30 min, and then attains a steady state, illustrating that the apparent discoloration of Orange II is just caused by the adsorption of Orange II on the surface of the Fe-Lap-RD catalyst, and no reaction occurred at all. With 1.0 g Fe-Lap-RD/L, 100 mM H_2O_2, and 2 × 8 W UVC (curve c), the discoloration of 2 mM Orange II is also very fast in the first 30 min due to adsorption of Orange II on the surface of the Fe-Lap-RD catalyst as mentioned above. After 30 min dark adsorption, when 2 × 8 W UVC were turned on, further discoloration is also very rapid. Complete discoloration of 2 mM Orange II is achieved after 120 min reaction, implying that Fe-Lap-RD catalyst exhibits a good photo catalytic activity in the discoloration of high concentration Orange II. The fast discoloration of 2 mM Orange II comes from the oxidation of Orange II by OH radicals generated from both heterogeneous and homogeneous photo Fenton reactions, which will be

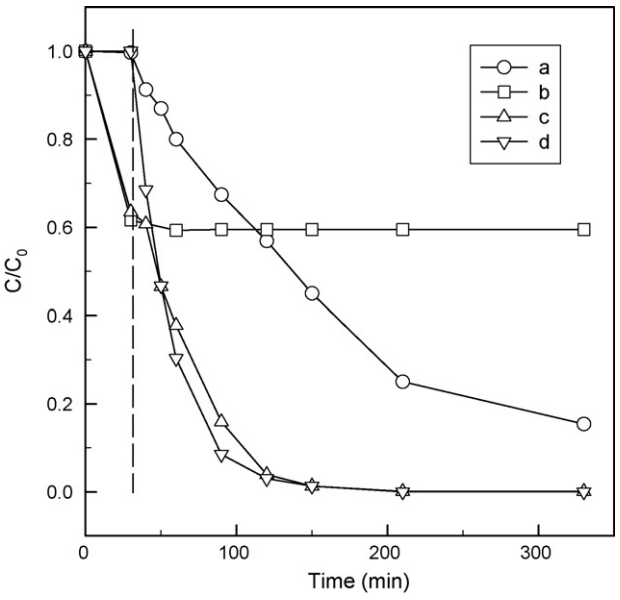

Fig. 1. Discoloration of 2 mM Orange II under different conditions: (a) 2 × 8 W UVC + 100 mM H_2O_2, (b) 1.0 g Fe-Lap-RD/L + dark, (c) 2 × 8 W UVC + 100 mM H_2O_2 + 1.0 g Fe-Lap-RD/L, and (d) 2 × 8W UVC + 10 mg Fe^{3+}/L + 100 mM H_2O_2.