Heterogeneous Fenton-like degradation of an azo dye reactive brilliant orange by the combination of activated carbon–FeOOH catalyst and H$_2$O$_2$

Jinhua Wu, Guanghui Lin, Ping Li, Weizhao Yin, Xiangde Wang and Bo Yang

**ABSTRACT**

The decoloration of an azo dye reactive brilliant orange (X-GN) by a heterogeneous Fenton system using activated carbon–FeOOH catalyst (AC–FeOOH) and H$_2$O$_2$ was studied. Under typical conditions (pH 7.0, H$_2$O$_2$ 10 mmol/L, AC–FeOOH 1.0 g/L and 30 °C), 98% decoloration rate of X-GN was achieved in 240 min. The decoloration efficiency of X-GN increased with higher H$_2$O$_2$ dosage, higher AC–FeOOH dosage and higher reaction temperature. Though the catalytic reaction was an acid driven process, a sufficient decoloration performance was still obtained in neutral and alkaline conditions. Kinetic studies suggested that the decoloration of X-GN followed a pseudo-first order reaction and the activation energy was 17.2 kJ/mol. Iron leaching from AC–FeOOH occurred during the reaction, but the decoloration efficiency of X-GN was still higher than 80% after four runs. The AC–FeOOH has a good stability and can be reused. Besides, the generation of massive iron-containing sludge can be avoided after reaction as the remaining ferric ions in the solution were less than 1 mg/L in this combined H$_2$O$_2$ and AC–FeOOH process.

**Key words** | activated carbon–FeOOH catalyst, heterogeneous Fenton, hydrogen peroxide, reactive brilliant orange

**INTRODUCTION**

Azo dyes are characterized by one or more azo groups as the chromophore in the molecular structure. Almost 50–70% of all dyes available on the market are azo dyes (Telke et al. 2008). They are widely used in textile, leather, food and printing industries and at least 2–10% of them are discharged into the water environment during their production and utilization (Neamtu et al. 2002; Carneiro et al. 2007). Azo dyes and their degradation products are carcinogenic to human beings and toxic to the hydrobios (Stylidi et al. 2004). Apparently, even in low concentrations and small quantities they will deteriorate the hydroenvironment and pose significant risks to public health. Therefore, the removal of azo dyes is an important aspect of wastewater treatment before discharge.

Various methods such as adsorption, coagulation, membrane separation and biodegradation have been investigated and developed to deal with azo dye wastewaters (Forgacs et al. 2004). However, each process has its own technical or economic limits. For example, pollutants can be removed effectively by adsorption, coagulation and membrane separation, but they are merely transferred from one phase to another causing secondary pollution. Biodegradation seems to be an inexpensive alternative to remove dyes from wastewater, but azo dyes are resistant to biodegradation in aerobic conditions and more toxic intermediates are generated in anaerobic conditions (van der Zee & Villaverde 2005).

Fenton reagent is an effective process for the treatment of azo dye wastewaters since it can be operated at room temperature and pressure (Ramirez et al. 2007). The HO$^\cdot$ produced by the interaction between Fe$^{2+}$ and H$_2$O$_2$ has a redox potential of 2.8 V and the ability to decompose most of the recalcitrant organic pollutants. However, the optimum pH for Fenton reactions is about 3, thus the requirement of a large amount of acid in influent and alkaline in effluent for neutralization will result in a high

**doi:** 10.2166/wst.2012.596
disposal cost (Valdes-Solis et al. 2007; Hanna et al. 2008). Besides, the conversion of Fe$^{3+}$ to Fe$^{2+}$ is so slow that a great deal of ferrous salt is required to maintain the concentration of Fe$^{2+}$ during the reaction (Martínez et al. 2005). The Fe$^{2+}$ containing sludge following a Fenton reaction after neutralization is a serious problem. These drawbacks limit the application of homogeneous Fenton processes in dye wastewater treatment (Hsueh et al. 2007).

To overcome these drawbacks, supporting Fe, Fe$_2$O$_3$ and their combination on porous materials were employed to replace Fe$^{2+}$ during Fenton reactions for the degradation of dye wastewaters (Daud & Hameed 2011; Panda et al. 2011). These catalysts have been proven to be effective and can be reused in Fenton processes because iron species are immobilized on heterogeneous supports (Kasiri et al. 2008). Goethite ($\alpha$-FeOOH) is another common ferric mineral in the natural environment. It has a nano-sized structure and is easily accessible to pollutants. Besides, the operation in the presence of goethite and H$_2$O$_2$ does not require a strict control of pH (Garrido-Ramírez et al. 2010). Compared to Fe and Fe$_2$O$_3$, $\alpha$-FeOOH may be more effective and has a more extended operational pH range in Fenton processes. However, to our knowledge, few researches about the decoloration of X-GN was selected as an objective pollutant because it is altered to AC–FeOOH after 12 h drying at 100 °C.

The X-ray diffraction (XRD) pattern of the catalyst was measured with a D8 ADVANCE X-ray diffractometer (Bruker, Germany) equipped with Cu Kα radiation at 40 kV and 40 mA. The iron species supported on the AC were primarily confirmed as $\alpha$-FeOOH according to three XRD peaks at 28.5°, 38.3° and 40.9° (Zhang et al. 2011). The results from X-ray fluorescence (XRF) (PANalytical PW-4400 spectrometer, Germany) analysis revealed that the content of iron in the AC-FeOOH was 3.3 wt%. N$_2$ adsorption at 77 K was measured with an ASAP 2020 surface area analyzer (Micromeritics, USA). The data depicted that the specific surface area, pore volume and pore size of AC were 541 m$^2$/g, 0.34 cm$^3$/g and 2.5 nm, and they decreased to 375 m$^2$/g, 0.29 cm$^3$/g and 1.9 nm in the AC–FeOOH.

**Experimental procedures**

Batch experiments were conducted in 300 mL conical flask reactors containing 250 mL solution with 60 mg/L X-GN (C$_{19}$H$_{12}$Cl$_2$N$_6$O$_7$S$_2$, MW = 571 g/mol). The initial pH value was adjusted to 7.0 by H$_2$SO$_4$ or NaOH. After the addition of 10 mmol/L H$_2$O$_2$ and 1.0 g/L AC–FeOOH, the flask was capped with a rubber plug and agitated in an isothermal shaker (130 r/min, 30 °C). All experiments were conducted in the dark to avoid the photochemical process. At regular intervals, a sample solution was withdrawn with a syringe and then filtered with a 0.45 μm membrane, followed by immediate analysis. Each experiment was carried out in triplicate and an average value was shown in this study. Batch tests were conducted on the basis of the above benchmark experiment to evaluate the effects of initial pH, H$_2$O$_2$ dosage, AC–FeOOH dosage and temperature on X-GN decoloration.

**Analysis method**

The concentration of X-GN was measured with a UV–vis spectrophotometer (Shimazu 2450) at the maximum absorbance wavelength of 479 nm. The decoloration efficiency was calculated according to Equation (1):

$$\text{Decoloration} = \frac{(C_0 - C_t)}{C_0} \times 100\%$$ (1)

where $C_0$ was the initial concentration of X-GN, and $C_t$ was the concentration of X-GN at reaction time $t$. The concentration of dissolved iron ions after reaction was measured by the o-phenanthroline colorimetric method (China NEPA 2002). The pH value was monitored by a pH meter
(PHS-3C, Sanxin, China). The morphology variation of the catalyst after reaction was analyzed by a Hitachi S-4500 Scanning electron microscope.

RESULTS AND DISCUSSION

Comparison experiments

The decoloration experiments were conducted with H$_2$O$_2$, AC–FeOOH and a combination of H$_2$O$_2$ and AC–FeOOH, respectively. As shown in Figure 1, no significant color removal was observed after 240 min reaction time in the H$_2$O$_2$ system, indicating that H$_2$O$_2$ did not contribute to the decoloration of X-GN. This was mainly because of the lower oxidation potential of H$_2$O$_2$ in comparison with HO• radical and HO$_2$ radical. In the AC–FeOOH system, about 21% color removal of X-GN was obtained, which was attributed to the adsorption of X-GN onto AC–FeOOH particles. However, in the AC–FeOOH/H$_2$O$_2$ system, it can be observed that 98% of the color in the solution was removed in 240 min. This was mainly due to the generation of HO• radicals as a result of the interaction between H$_2$O$_2$ and AC–FeOOH. The reaction mechanism could be described by the following equations (Kwan & Voelker 2003):

$$\text{Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(II)} + \text{HO}_2^- + \text{H}^+ \quad (2)$$

$$\text{Fe(OH}_2)^{2+} \rightarrow \text{Fe(II)} + \text{HO}_2^- \quad (3)$$

$$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{OH}^- + \text{HO}^+ \quad (4)$$

$$\text{HO}^+ + \text{X - GN} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{intermediates} \quad (5)$$

Effect of operational parameters

The effect of initial pH on the decoloration of X-GN was studied over a pH range of 2.0–9.0 (Figure 2(a)). When the initial pH value decreased from 9.0 to 3.0, the decoloration rate of X-GN increased from 61 to 100% within 90 min. But it decreased to 94% as the initial pH value further decreased to 2.0. It is apparent that the decoloration of X-GN was highly pH-dependent. This was related to more HO• radicals being available to attack the dye molecules in the solution with a lower pH, since H$_2$O$_2$ was increasingly unstable and it would be decomposed to produce H$_2$O and O$_2$ instead when the pH value was higher than 4.0 (Du et al. 2008). Besides, the ferrous ions might precipitate in alkaline conditions to form iron hydroxide (Fe(OH)$_3$) or hydrous ferric oxide (Fe$_2$O$_3$·nH$_2$O) (Liang et al. 2009). These iron precipitates have low efficiency to activate H$_2$O$_2$ to produce HO• radicals (Kang & Hwang 2000). However, pH below 2.0 was not suitable for the degradation of X-GN in this AC–FeOOH/H$_2$O$_2$ system. Actually, H$^+$ is easily captured by H$_2$O$_2$ to produce H$_3$O$_2$+ at a lower pH, thus the reaction between H$_2$O$_2$ and Fe(II) is restrained (Gogate & Pandit 2004). More ferric ion was observed at lower pH value after the reaction (data not shown). It was found to be 1.21, 1.12, 0.85, 0.49 and 0.27 mg/L corresponding to an initial pH value of 2.0, 3.0, 5.0, 7.0 and 9.0, respectively. Since 98% decoloration efficiency of X-GN was achieved at initial pH 7.0 in 240 min, the initial pH 7.0 was selected for further experiments.

In comparison with conventional Fenton processes, two obvious advantages were found in this AC–FeOOH/H$_2$O$_2$ system. Primarily, a sufficient performance was still obtained in neutral and alkaline conditions. Therefore, the addition of a large amount of acid can be avoided when AC–FeOOH is used as catalyst, since the effluent of dye-containing wastewaters is alkaline in many industries. Secondly, the generation of massive iron-containing sludge can be avoided after reaction as Fe(III) was regenerated (Equations (2) and (3)) and the remaining ferric ions in the solution after reaction were nearly negligible (less than 0.5 mg/L at pH 7.0) in this process.

The effect of H$_2$O$_2$ dosage on the decoloration of X-GN was investigated by varying the initial H$_2$O$_2$ concentration...
from 5 to 20 mmol/L. As shown in Figure 2(b), the decoloration efficiency of X-GN increased from 89 to 97% in 240 min with an increase of \( \text{H}_2\text{O}_2 \) dosage from 5 to 10 mmol/L, because more HO• radicals were generated and available at higher \( \text{H}_2\text{O}_2 \) dosages. However, the decoloration efficiency of X-GN decreased slightly when the \( \text{H}_2\text{O}_2 \) dosage was further increased to 15 and 20 mmol/L. This was because the HO• radicals could be scavenged through side reactions (Equations (6) and (7)) at higher \( \text{H}_2\text{O}_2 \) dosages:

\[
\text{H}_2\text{O}_2 + \cdot\text{HO} \rightarrow \text{H}_2\text{O} + \cdot\text{HO}_2 \tag{6}
\]

\[
\cdot\text{HO}_2 + \cdot\text{HO} \rightarrow \text{H}_2\text{O} + \text{O}_2 \tag{7}
\]

The concentrations of ferric ions after reaction were between 0.46 and 0.52 mg/L, indicating that the variation of \( \text{H}_2\text{O}_2 \) concentration did not affect the iron leaching from AC–FeOOH significantly. Based on the aforementioned, 10 mmol/L was chosen as the optimum \( \text{H}_2\text{O}_2 \) loading in the present study.

The effect of AC–FeOOH dosage on the X-GN decoloration was conducted by changing the initial AC–FeOOH dosage from 0.6 to 1.2 g/L, and the experimental results are depicted in Figure 2(c). On increasing the AC–FeOOH dosage from 0.6 to 1.0 g/L, X-GN decoloration increased from 82 to 98% in 240 min. This was attributed to more active sites available on the AC–FeOOH to decompose \( \text{H}_2\text{O}_2 \) into HO• radicals. However, the decoloration efficiency declined to 96% with a higher catalyst dosage of 1.2 g/L. This was probably due to the parallel reaction between excessive Fe(II) and HO• radicals (Equation (8)).

\[
\text{Fe}(\text{II}) + \cdot\text{HO} \rightarrow \text{Fe}(\text{III}) + \cdot\text{OH}^- \tag{8}
\]

Though the concentration of ferric ion after reaction increased with catalyst dosage and was recorded as 0.32, 0.41, 0.49 and 0.56 mg/L at a catalyst dosage of 0.6, 0.8, 1.0 and 1.2 g/L respectively, it was also nearly negligible as compared to that of more than 10 mg/L in homogeneous Fenton processes (Chen et al. 2010). The optimum catalyst dosage was determined as 1.0 g/L in the present study.

Batch experiments were conducted between 30 and 70 °C to study the influence of temperature on the decoloration of X-GN. As shown in Figure 2(d), the decoloration efficiency of X-GN increased from 82 to 100% with an increase of temperature from 30 to 70 °C in 120 min. A relatively high temperature was favorable to this catalytic reaction.
reaction, because both kinetic constants for the HO· radical generation and Fe(III)/Fe(II) conversion increased with temperature (Herney-Ramirez et al. 2008). In addition, the temperature of dye wastewater effluents is often around 40°C, so the AC–FeOOH/H2O2 process is suitable to treat dye wastewater owing to its efficient decoloration and energy conservation.

Kinetics study indicated that AC–FeOOH/H2O2 decoloration is a pseudo-first order reaction, which can be expressed as Equation (9).

\[ \ln \left( \frac{C_t}{C_0} \right) = -kt \]  

(9)

where \( C_0 \) was the initial concentration of X-GN; \( C_t \) was the concentration of X-GN at reaction time \( t \); \( k \) was the pseudo-first order rate constant. The \( k \) was determined as 0.0148 \( (R^2 = 0.9888) \), 0.0222 \( (R^2 = 0.9738) \), 0.0268 \( (R^2 = 0.9962) \), 0.0378 \( (R^2 = 0.9737) \) and 0.0472 \( (R^2 = 0.9967) \) min\(^{-1}\) at 30, 40, 50, 60 and 70°C, respectively. Based on the \( k \) at five temperatures, the activation energy of X-GN degradation by the combination of AC–FeOOH and H2O2 can be obtained according to the Arrhenius equation:

\[ \ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A \]  

(10)

where \( E_a \) was the activation energy (kJ/mol); \( R \) was the gas constant (0.008314 kJ/(mol·K)); \( T \) was the absolute temperature (K); \( A \) was a frequency factor (min\(^{-1}\)). It can be observed that there is a strong linear relationship between \( \ln k \) and 1/\( T \) (Figure 2(d)). The activation energy was calculated to be 17.2 kJ/mol, which was consistent with the result of Karthikeyan et al. (2011), indicating that the degradation of X-GN by the catalytic reaction between AC–FeOOH and H2O2 was relatively favorable, since the ordinary thermal reaction energy is between 60 and 250 kJ/mol (Chen & Zhu 2013; Karthikeyan et al. 2011).

**Change of X-GN and catalyst during reaction**

The change in the UV–visible spectrum for the decoloration of X-GN at different reaction times is presented in Figure 3(a). The absorption peak at 479 nm was the characteristic peak position of the chromophore structure of X-GN. Obviously, it disappeared after a reaction time of 240 min. Meanwhile, the peak at 298 nm, which was assigned to the naphthalene ring of X-GN, was also eliminated in 240 min. This implied that the N=N group and the naphthalene ring of X-GN were markedly destroyed. The absorbance between 200 and 250 nm increased early in the reaction, but began to decrease after 60 min treatment, suggesting that intermediate products were generated and mineralized to a certain extent during the catalytic degradation of X-GN by the combination of H2O2 and AC–FeOOH.
The change of the AC–FeOOH was analyzed by scanning electron microscopy (SEM) after four runs and is shown in Figures 3(b) and 3(c). After each run, the AC–FeOOH was filtered and dried for the next run. The surface of the treated AC–FeOOH was much more coarse than that of the fresh one. This coarse and unstable structure may lead to an increase of ferric ion leaching and a decrease of decoloration efficiency of X-GN. Actually, the decoloration efficiency of X-GN decreased from 98 to 81% and the ferric ion in the solution after reaction increased from 0.49 to 0.75 mg/L after four runs. However, the decoloration efficiency of X-GN still remained at 80% after four runs, indicating that the AC–FeOOH has a good stability and can be reused for successive treatments.

CONCLUSIONS

In this work, AC–FeOOH catalyst was prepared and used for the degradation of an azo dye X-GN through heterogeneous Fenton-like processes. The decoloration efficiency of X-GN increased with higher H2O2 dosage, higher AC–FeOOH dosage and higher reaction temperature. This reaction followed a pseudo-first order reaction and the activation energy was 17.2 kJ/mol. Although this Fenton-like reaction was an acid driven process, a sufficient decoloration efficiency was still obtained in neutral and alkaline conditions. The low leaching of ferric ion and the high performance of the catalyst during the cycle test also indicated that the AC–FeOOH catalyst is able to extend and facilitate the application of the heterogeneous Fenton-like process in azo dye wastewater treatment.

ACKNOWLEDGEMENTS

The authors thank the National Natural Science Foundation of China (50708039), the National High-Tech Research and Development Program of China (863 Program; Grant 2009AA063902) and the Fundamental Research Funds for the Central Universities (2012ZZ0047).

REFERENCES


Kwan, W. P. & Voelker, B. M. 2005 Rates of hydroxyl radical generation and organic compound oxidation in...


