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Solar active fire clay based hetero-Fenton catalyst over a wide pH range for degradation of Acid Violet 7

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Abstract

Fe(III) immobilized fire clay (Fe-FC) was prepared using ferric nitrate by solid state dispersion method and this hetero-Fenton catalyst was applied for the degradation of Acid Violet 7 (AV 7) under natural sunlight. The 26% ferric nitrate loaded fire clay was found to be most efficient. The experimental conditions such as solution pH, H_2O_2 concentration for efficient degradation of AV 7 have been determined. Unlike Fenton catalyst, Fe-FC is photoactive over a wide pH range of 3–7. This catalyst was found to be stable and reusable. The GC-MS analysis of experimental solutions during irradiation revealed the formation of 2,8-diaminonaphthalene-1,3,6-triol, 8-aminonaphthalene-1,2,3,6-tetrol, 2-aminonaphthalene-1,3,6,8-tetrol and 2-aminobenzene-1,3-diol/5-aminonbenzene-1,3-diol/2-aminobenzene-1,4-diol as intermediates. The 26% ferric nitrate loaded fire clay was characterized by XRD, ICP-AES, BET surface area, FT-IR, SEM-EDS and UV-DRS studies.

Key words: hetero-Fenton degradation; Acid Violet 7; fire clay; wastewater treatment; solar light

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Introduction

The Fenton process has a long-established credibility to generate the powerful oxidant, hydroxyl radical (Walling, 1975; Fenton, 1894), which is useful particularly in the field of environmental remediation for non-biodegradable pollutants. Recently photo-Fenton process has been widely used since Fe^{2+} ions can be regenerated by photolytic reduction of Fe^{3+}. For photo-Fenton process, use of artificial UV light sources requires electrical energy for the production of photons (Pérez et al., 2002) and therefore more environmentally benign and cost-effective methods are desirable. As an alternative to UV light sources, solar light can be successfully used since solar energy is an abundant natural energy source (Robert et al., 2004; Gumy et al., 2005). The Fenton reagent (a mixture of Fe^{2+} and H_2O_2) is one of the most active systems for the oxidation of organics in water. Its reactivity is due to the *in situ* generation of highly oxidative hydroxyl radicals (•OH) (Eqs. (1) and (2)).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH + {}^{-}OH \quad (1)$$

$$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + \cdot OH + H^+ \quad (2)$$

However, the traditional homogenous Fenton reaction uses a high concentration of iron that must subsequently be removed and can result in sludge. Additionally, it requires acidic conditions, typically below pH 3.0, which is unfavorable in practice because of the costs of acidification during processing and neutralization after treatment. Therefore, an immobilized iron catalyst, which can promote a heterogeneous Fenton process under less acidic conditions, is an important objective of research in this area (Haber and Weiss, 1934; Barrault et al., 2000; Bozzi et al., 2003; Carriazo et al., 2003, 2005; Centi et al., 2000).

The Fe(III) ions have been immobilized on various supports including nafion membrane (Fernandez et al., 1999; Parra et al., 2003), alginate gel beads (Fernandez et al., 2000), laponite clay (Feng et al., 2006), bentonite (Chen and Zhu, 2007), neutral alumina (Muthuvel and Swaminathan, 2007, 2008), cation exchange resin (Lv et al., 2005) and zeolites (Neamtu et al., 2004a, 2004b). Being inexpensive and widely available, clays represent an attractive substrate for iron immobilization. The use of clays as catalyst and catalyst support has received considerable attention (Garrido-Ramírez et al, 2010; Herney-Ramireza et al., 2010; Feng et al., 2003). Fire clay is a sedimentary material consisting of fine particles of aluminium hydrosilicates with a layer structure and it is free from fluxes such as larger quantities of iron, alkaline earth, alkalis and excess silica. Its main constituents are minerals of the kaoline group.

Azo dyes have been used increasingly in industries because of their ease and cost effectiveness in synthesis compared to natural dyes. These dyes constitute the largest group over thousands of commercial dyestuffs and are commonly used for textiles dyeing, paper printing, food

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and cosmetic coloring. Dye industrial wastewater contains significant concentration of dye leading to a high level of total organic content and of color.

In continuation of our earlier work on the development of hetero-Fenton catalysts for a wide pH range, we herein report the preparation and characterization of Fe(III) encapsulated Fireclay and its photocatalytic activity on the degradation of Acid Violet 7 (AV 7).

1 Experimental

1.1 Materials

Fireclay (FC) was obtained from Government Ceramic Institute, Tamilnadu, India. The chemical composition (wt.%) of the clay (main elements) is SiO_2 70.5; Al_2O_3 15.7; Fe_2O_3 0.1; MgO 0.4. Cation exchange capacity of the clay is 48.8 Meq/100 g. Acid Violet 7 (C.I 18055) (s.d. fine chemicals), H_2O_2, Fe $(NO_3)_3 \cdot 7H_2O$, H_2SO_4 and NaOH (Qualigens) were of analytical grade. All the solutions were prepared with deionized water.

1.2 Apparatus

X-ray diffraction (XRD) pattern (Bruker, Germany) of the catalysts were recorded by PANalytical X-ray diffractometer having a graphite crystal diffracted monochromater with a source of Cu-Kα radiation and NaI (TI) scintillation detector (Bruker, Germany). The iron content of the catalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis by ISA JOHIN YUON 24 MODEL spectrometer (ARCOS from M/s. Spectro, Germany). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by Nicolet Avatar-36 (Nicolet Instrument Corporation Madison, USA). Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) images were taken by JSM-5610 series (OXFORD Instrument, Japan). BET surface area and total pore volume measurements were made by micromeritics ASAP 2020 unit. A PerkinElmer Lambda 35 UV/Vis spectrometer (USA) equipped with an integrated sphere was used to record the diffused reflectance spectra (DRS). The baseline correction was performed using a calibrated reference sample of barium sulfate. The reflectance spectra of the samples were analyzed under ambient conditions in the wavelength range of 200 to 1100 nm. For gas chromatography analysis, PerkinElmer GC-9000 (Varian, the Netherlands) with a capillary column of DB-5 and flame ionization detector was used. Gas chromotography-mass spectrometry (GC-MS) analysis was carried out using GC model: Varian GC-MS-Saturn 2200 Thermo (Varian, the Netherlands) capillary column VF5MS (5% phenyl–95% methylpolysiloxane, 30 m length, 0.25 mm internal diameter, 0.25 μm film thickness), temperature of column range from 50 to 280°C (10°C/min) and injector temperature 250°C.

1.3 Preparation of fire clay-Fe(III) (Fe-FC) catalyst

Four different weight percent of (13%, 20%, 26% and 31%) ferric nitrate solutions were prepared in 60/40 ethanol-water medium. Five grams of fire clay was mixed with appropriate concentration of ferric nitrate solution. The mixed suspension was stirred for 4 hr at room temperature. The product was centrifuged and washed several times with water. Then it was dried at 120°C for one hour. The Fe(III) loaded fireclay (Fe-FC) catalyst was obtained as a fine powder.

1.4 Photocatalytic activity studies

In all cases 50 mL of the dye solution containing appropriate quantity of the Fe-FC and H_2O_2 suspensions were used. The suspension was stirred for 10 min in dark and then it was irradiated. Dye solution was continuously aerated by a pump to provide oxygen and for complete mixing of reaction medium. At specific time interval, 2 mL of the sample was withdrawn and centrifuged to separate the catalyst. One milliliter of the centrifugate was diluted to 10 mL and its absorbances at 306 and 523 nm were measured. The absorbance at 523 nm is due to color of the dye and it was used to monitor the decolourization. The absorbance at 306 nm represents the aromatic content of AV 7 and the decrease in absorbance at 306 nm indicates the degradation of aromatic ring. Mineralization of dye was confirmed by the formation of $CaCO_3$ when the evolved gas (carbon dioxide) during the reaction passed into limewater.

UV spectral analysis was done using UV-Visible spectrophotometer (UV-1650 PC, Shimadzu, Japan). Solar light intensity was measured using LT Lutron LX-10/A digital Lux meter for every 10 min and the average light intensity over the duration of each experiment was calculated. The sensor was always set at the position of maximum intensity. The intensity of solar light (1100 × 100 lux) was nearly constant during the experiments.

The photocatalytic degradation of AV 7 containing iron-immobilized catalyst obey pseudo-first order kinetics. At low initial dye concentration the rate expression is given by

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k'C \tag{3}$$

where, k' is the pseudo-first order rate constant, C (mol/L) is the concentration of AV7 and t (min) is the irradiation time. The dye was adsorbed onto the iron immobilized catalyst surface and adsorption-desorption equilibrium was reached in 30 min. After adsorption, the equilibrium concentration of the dye solution was determined and it was taken as the initial dye concentration for kinetic analysis. Integration of Eq. (3) gives Eq. (4).

$$\ln\left(\frac{C_0}{C}\right) = k't \tag{4}$$

where, C_0 (mol/L) is the equilibrium concentration of dye at t = 0 and C (mol/L) is the concentration at time t. Pseudo-first order rate constant k' was determined from the plot of $\ln C_0/C$ vs t.