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Catalytic oxidation of Methyl Orange by an amorphous FeOOH catalyst developed from a high iron-containing fly ash

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ABSTRACT

Heterogeneous photo-Fenton process using an amorphous FeOOH as catalyst was studied to degrade Methyl Orange (MO) dye in aqueous solution. The amorphous FeOOH was prepared by dissolution and precipitation using a high iron-containing fly ash as raw material. The ash not only provided iron source but also acted as a supporter of amorphous FeOOH. Coating the fly ash particles with the amorphous FeOOH significantly enhanced the removal of MO, and 2.5 g of catalyst was sufficient to degrade 50 mg MO from 1 l of aqueous solution at pH 7.0 after 80 min. Oxidant concentration, solution pH, UV/dark/sunlight and recycling of the catalyst were investigated in order to evaluate the photo-Fenton effects. Moreover, variations of particle size before and after preparation, separation of solid–liquid and stability of the amorphous FeOOH in the catalyst were studied. It was testified that the amorphous FeOOH on the surface of fly ash was stable and the Fenton catalyst was easily separated from the aqueous system.

1. Introduction

The Fenton reaction has its own unique advantage in the degradation of pollutants as one of advanced oxidation processes (AOPs) because its reagents are environmentally benign, cheap and relatively easy to obtain and handle. The traditional homogeneous Fenton reaction works only in the pH range of 2.0–4.0 and tends to be highest at around pH 3.0 and then decreased with increasing pH, for example, the Fenton process nearly comes to halt as the pH increases from 3.0 to 7.0 when *p*-hydroxybenzoic acid was degraded in the system of homogenous Fenton [1]. For overcoming the above disadvantages of the homogeneous Fenton process, the heterogeneous Fenton reaction with aid of light irradiation was developed.

According to previous studies, some crystalline iron hydroxides/oxides (α-FeOOH, γ-FeOOH and γ-Fe_2O_3) [2–5] and supported iron compounds [6–10] as photo-Fenton catalysts have been intensively studied and are thought to be promising effective catalysts in the heterogeneous system. Briefly, their effectiveness is attributed to the production of surface iron complex (e.g. surface Fe (IV) species) and hydroxyl radicals ($HO^\bullet$) when UV irradiation of the surface broke chemical bond. Then the highly oxidized and unstable surface iron complex reacts with water to form a further $HO^\bullet$ [2]. Thus, the catalyst experiences an iron cycling on the surface without significant diffusion into the solution phase.

The free hydroxyl radicals are powerful, non-selective oxidants with the ability of decomposing almost all organic contaminants into carbon dioxide and water in aqueous solution, including dyes [8–10].

To our knowledge, however, amorphous FeOOH used as photo-Fenton reagent has not been attempted to degrade pollutants although its surface area is higher than the crystalline iron hydroxides. That is because the amorphous FeOOH is merely available as fine powder or exists as gel or suspension in the solution, hence it is difficult to be separated entirely from the solution. Another shortage of amorphous FeOOH is that it tends to form crystalline iron oxides in the preparation process, which may greatly reduce its degradation capacity since its surface area is greatly diminished, thus a stable and easily separated amorphous FeOOH photo-Fenton catalyst is desired.

The aim of this study was to investigate an amorphous FeOOH photo-Fenton reagent prepared by a high iron-containing fly ash (HICFA). The iron oxide content in this fly ash was as high as 17.52% and the amorphous FeOOH supported on the fly ash particles was prepared by the rearrangement of iron oxide contained in the fly ash.

Wastewater released from textile, painting, leather, printing and photography industries contains some recalcitrant pollutants, especially synthetic dyes, and the presence of small amounts of dyes (below 1 ppm) is clearly visible, and greatly influences the water environment [11]. Besides the aesthetic problem, dyes in wastewater limit the possible use of water and reduce the efficacy of the microbial wastewater treatment because they may be toxic to microorganisms. In this study, Methyl Orange (MO, Scheme 1) dye was selected as a model hydrocarbon due to its environmen-

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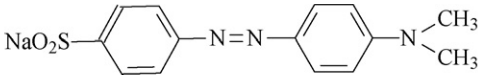

Scheme 1. Molecular structure of MO.

tal significance, ease of analysis, and relative solubility in water. The effects of important variables on the degradation of MO were investigated. This study was more concerned about the operational performance of the amorphous FeOOH photo-Fenton reagent for treating the wastewater, so the solid–liquid separation, variations of particle size before and after preparation, stability of amorphous FeOOH and recycling efficiency were investigated in detail.

2. Experimental details

2.1. Materials

Fly ash, a byproduct from power station, is one of the industry solid wastes in China, and the high iron-containing fly ash in this study was sampled from Gaobeidian thermal power plant (4 MW × 200 MW) located in Beijing (China). The ash was collected by an electrostatic precipitator after the pulverized coal burnt in the cyclone furnace boiler. The fly ash contains element oxides such as SiO_2 29.33%, Al_2O_3 25.70%, Fe_2O_3 17.52%, CaO 22.17%, MgO 1.60%, SO_3 4.15%, K_2O 0.56%, Na_2O 1.81% and its Loss on Ignition (LOI) is 0.27%.

MO, H_2O_2 (30%), $FeCl_3$ (AR) and diethyl ether (AR) were purchased from Beijing chemical works. Stocking solution containing 1000 mg l^{-1} of MO was directly dissolved from pure MO, and MO working solutions were freshly made by diluting stocking solution with distilled water. HCl (1 M, 0.1 M), and NaOH (1 M, 0.1 M) solutions were prepared for pH adjustment.

2.2. Preparation of photo-Fenton catalyst and analysis methods

The photo-Fenton catalyst was prepared by dissolution and precipitation using the high iron-containing fly ash as the raw material. The element Fe in the fly ash was dissolved into the acidic solution, then precipitated as the amorphous FeOOH and simultaneously deposited on the surface of the residual ash particles. The detailed depiction of synthesis process was presented in a previous report [12]. Briefly, the catalyst powder was prepared according to the following procedure: firstly, 3.0 g of the raw fly ash was added into 250 ml of water, and the mixture was stirred and heated to 95 °C for 1 h to remove some alkali and alkaline earth elements in the fly ash, then the insoluble material was filtrated and dried at 100 °C for 2 h. Secondly the pretreated fly ash was contacted with 100 ml of 1 M HCl solution, vibrated (200 r/min) in a rotary shaker (THZ-100, Nanjing chemical apparatus Inc, China) for 2 h and placed steadily at 60 °C for 0.5 h. Thirdly, 1 M NaOH solution was added dropwise into the solution until the final pH was adjusted to about 6.0 (except where otherwise specified). The mixture continuously vibrated for 1 h and aged at 75 °C for 3 days (except where otherwise specified). Finally, the slurry was dewatered by centrifugation and then dried at 75 °C for 24 h. Upon cooling, the composite solid was broken to separate the powders in the carnelian mortar, and afterwards stored in the capped polyethylene bottle for use.

The X-ray diffraction (XRD) patterns of the catalyst were obtained using X-ray diffractometer (Philips PW 1700, Holand) to examine the change of crystalline phase and the operating conditions were 45 kV and 250 mA, using Cu Kα radioactive source. The surface morphology was obtained using scanning electron micrograph (SEM) (Hitachi S–3000N, Japan). The technology of laser particle size (LPS) was used to analyze the particle size distribution of raw fly ash and the catalyst by laser particle sizer (Master size 2000, Malvern Co, UK). The BET (Brunauer–Emmet–Teller) specific surface area was determined by fitting the linear portion of the BET plot to BET equation, and average pore size was calculated based on the desorption plot of N_2 adsorption–desorption isotherm using the Barrett–Joyner–Halenda (BJH) method (Micrometritics ASAP 2000, USA). The absorbance of MO solution was examined by the UV–vis spectroscopy (UV-2450, Shimadzu, Japan). The iron leaching iron concentration was examined by inductively coupled plasma optical emission spectrometer (ICP–OES) (PerkinElmer OPTIMA 2000, USA).

2.3. Experimental procedure of photo-Fenton degradation of MO

The UV degradation experiments were carried out inside a 600 m × 550 mm × 450 mm stainless box with a door in one side for operating. A UV lamp (GY-250, TIANMEI light source of Beijing, China) with the main emission of 365 nm positioned in the center of reactor was used as an irradiation source, and a series of 100-ml quartz flasks were employed as photo-Fenton reaction vessels. About 21 cm^2 of surface area in the flasks was directly exposed to the irradiation light, and the photo flux near the flasks was about 60 W m^{-2} (UVA radiation meter, photoelectric instrument factory of Beijing Normal University, China). The flasks were stirred magnetically during irradiation. In the experiments, the effects of solution pH (from 5.0 to 7.0), contact time (from 120 to 180 min), irradiation light (sunlight, darkness, UV) and H_2O_2 concentration (0, 5.26, 15.8 and 26.3 mM) were examined so as to optimize operation conditions. The solution was sampled and taken out from the reactor at desired time intervals, and then centrifuged to separate solid from the solution. For avoiding any possible effect of further reaction caused by the $HO^{\bullet}$ after centrifugation, the supernatant was analyzed immediately by UV–vis spectroscopy to test the degradation of MO.

The wavelength of 460.5 nm, which is the maximum absorbance wavelength registered experimentally and is ascribed to the azo bond ($-N \equiv N-$) of the Methyl Orange molecule, was used for evaluation of the MO photodegradation. The photocatalytic degradation conversion was calculated with the following formula without concerning the degradation intermediates,

$$\eta_D = \frac{\mathrm{Abs}_0 - Abs_t}{\mathrm{Abs}_0} \times 100\% \qquad (3)$$

where η_D is the degradation ratio of MO, Abs_0 and Abs_t are the absorbency of MO solution at initial time and after irradiated in t time at 460.5 nm, respectively. Moreover, the experimental data are fitted by applying a pseudo-first-order model $\ln(\mathrm{Abs}_t/\mathrm{Abs}_0) = -kt$ to determine an observed rate constant (k) of MO in the experiments.

In addition, the solar induced oxidation of MO was performed at Research Center for Eco-Environmental Sciences (RCEES) parking lot (39°48′N; 116°28′E), Chinese Academy of Science (CAS) in Beijing, China. The environmental temperature in the experimental time was 15–18 °C, and the reaction temperature was controlled at 25 °C. The solar irradiation intensity was in range of 540–600 W m^{-2} with an average UV irradiation intensity 6 W m^{-2}. Darkness was realized by wrapping the flask using aluminum foils.

3. Results and discussion

3.1. Characterization of the catalyst

The SEM image of the catalyst is shown in Fig. 1. The amorphous FeOOH loaded on the sphere was irregular porous structure, and the size of catalyst mainly ranged from 15 to 30 μm. The inner sphere in the catalyst was the residual fly ash after acidized by HCl solution and then coated by the amorphous FeOOH when iron precipitated from solution. So the high iron-containing fly ash not