Journal of Photochemistry and Photobiology A: Chemistry 237 (2012) 31–37

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photodegradation kinetics of 2,6-dimetylphenol by natural iron oxide and oxalate in aqueous solution

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ARTICLE INFO

Article history:
Received 28 July 2011
Received in revised form 25 March 2012
Accepted 31 March 2012
Available online 6 April 2012

Keywords:
2,6-Dimethylphenol
Photodegradation
Natural iron oxide
Oxalic acid
Dissolved Fe–oxalate
Hydroxyl radicals

ABSTRACT

Heterogeneous photodegradation of 2,6-dimethylphenol (2,6-DMP) in the natural iron oxide (NIO) system with oxalic acid under UV irradiation was investigated. The NIO was characterized by X-ray diffraction (XRD), X-ray fluorescence and Brunauer–Emmett–Teller (BET) methods. The XRD pattern of NIO showed a mixed crystal structure. In order to show the effect of temperature on the structure of NIO, the last one was calcined at 800 °C and 1000 °C. The XRD patterns of calcined iron oxides at 800 °C (NIO/800) and 1000 °C (NIO/1000) depict the conversion from mixed crystalline hematite to completely pure crystalline hematite. The experiments showed that the most effective catalyst for degradation of 2,6-DMP is NIO in presence of oxalate. The dependence of 2,6-DMP degradation was attributable to the formation of the dissolved Fe–oxalate in the solution and the adsorbed Fe–oxalate on the surface of natural iron oxide. The photodegradation of 2,6-DMP depends also on the oxalate and pH. The optimal initial concentration of oxalic acid was found to be 5×10^{-3} M. The results demonstrated that the optimal pH value should be in the range of 3–4. The use of 2.0% of isopropanol as a scavenger confirmed the intervention of hydroxyl radicals in the photodegradation of 2,6-DMP. Furthermore, an important effect of oxygen was observed.

1. Introduction

Nowadays the removal of aromatic compounds in waste waters which may interfere with the normal functioning of endocrine systems has been an important challenge. The application of treatment methods such as adsorption, chemical treatments, membrane technologies or advanced oxidation processes (AOPs) have appeared as an important alternative for the efficient abatement of organic pollutants. AOPs, like the one presented in this study, are characterized by the generation of hydroxyl radicals, very strong oxidizing species that unselectively mineralize most of the contaminants present in effluent water. The heterogeneous iron oxide-oxalate system has been used as a great source of oxidative radicals.

Iron oxides are common compounds which are widespread in nature and readily synthesized in the laboratory, they are found in soils and rocks, lakes and rivers, on the seafloor, in air and organism [1]. Major iron oxides include goethite (α-FeOOH), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), lepidocrocite (γ-FeOOH) and magnetite (Fe_3O_4) show semiconductor properties with a narrow band gap of 2.0–2.3 eV and could be photoactive under solar irradiation [2]. Iron oxides promote photolysis of various adsorbed species including amino phenols [3] alcohols and amines [4] and carboxylic acids [5,6]. Among the family of polycarboxylic acids, oxalic acid is one of the most active members. Oxalic acid, mainly secreted by plant roots [7] or formed by incomplete combustion of hydrocarbons [8,9], is ubiquitous in soil, water and atmosphere. The solubility of iron in surface waters is controlled in part by photochemical process through light-induced reductive dissolution of iron(III)(hydr)oxides in the presence of ligands which are metastable with respect to Fe(III) such as oxalates.

In nature, iron, oxalic acid and sunlight can establish a homogeneous photo-Fenton-like system where iron exists in a dissolved form or a heterogeneous photo-Fenton-like system where iron is in a solid form [10]. The heterogeneous Fe(III)-oxalate system should be more applicable to the natural environment, because the iron species are mostly present as amorphous or (hydr)oxides [10]. In the 1990s several research groups [11–15] studied the mechanisms of iron (hydr)oxides dissolution in aqueous oxalate solution. The chemical adsorption of oxalic acid first occurs on the surface of iron oxide leading to the formation of Fe–oxalate complexes, and simultaneously the non-reductive/reductive dissolution of iron oxide takes place [16–20]. Light irradiation can greatly enhance the reductive dissolution of Fe(III)–oxalate complexes, yielding Fe(II) and oxalate radical $(C_2O_4)^{\bullet -}$ [13–20].

In this study 2,6-dimethylphenol (2,6-DMP) or 2,6-xylenol was selected as a model pollutant. This xenobiotic compound is the sixth isomer of xylenols wich represent an important component of the phenolic substances in coal tar creosote, a mixture used widely as

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http://dx.doi.org/10.1016/j.jphotochem.2012.03.023

a wood preservative. The xylenols represent 35% in weight of this mixture (the mixture being composed of 85% of polycyclic aromatic hydrocarbons, of 10% of phenolic compounds and 5% of heterocyclic compounds of nitrogen, sulfur or oxygen) [21]. They are thus likely to be in considerable quantity in the environment. Accumulation of phenolic compounds often leads to damage of cell structures and disturbs the function of tissues. For example, an alarming symptom is the change of the oxygen affinity of hemoglobin under the influence of 4-chloro-2-methylphenoxyacetic acid (MCPA) and 2,4-xylenol [22]. The investigation of viable methods of treatment of polluted waters containing trace amounts of xylenols is, therefore, of environmental interest. In this work we have used a natural iron oxide which is provided from the iron deposits from Chaabet-El-Ballout which is located in North-East Algerian. This last is an important mountainous chain which is prolonged towards the North-East in Tunisia. The iron deposits of Chaabet-El-Ballout covers an area of about 5 km^2. The analysis of iron deposits revealed that they are mostly composed of hematite.

The present study reports on laboratory experiments carried out with the natural iron oxide (NIO) and oxalate as a model system under UV irradiation. The process was applied in order to improve the degradation of 2,6-DMP, to the best of our knowledge, the photocatalytic degradation of 2,6-DMP in an iron oxide–oxalate complex system has not been investigated up until now. The effects of various parameters, such as the amount of the photocatalyst, initial concentration of oxalic acid and pH value on the photocatalytic degradation of 2,6-DMP were studied to determine the optimum treatment conditions. The oxidation of 2,6-DMP was also compared in the presence and absence of O_2.

2. Materials and methods

2.1. Materials

2,6-dimethylphenol was supplied by Reidel-de Haën (purity greater than 99%). NaOH (98%) and methanol (99%) was provided by Carlo Erba Reagenti. HCl (37%) Merck, ammonium acetate (98%), acetate sodium (99%), acetic acid (99.5%) and sulfuric acid (98%) provided by Panreac. 1,10 phenantroline Fluka (>99%), percloric acid 98%, and Oxalic acid (99.5%), Prolabo. The natural iron oxide (NIO) was washed several times with distilled water and dried at 45 °C. The NIO/800 and NIO/1000 samples were calcined at two different temperatures of 800 °C and 1000 °C for 2 h.

2.2. Irradiation procedure

The irradiation experiments were carried out in a self-constructed Pyrex photoreactor (diameter of 2 cm) with a cooling water jacket placed in an elliptical stainless steel chamber. A fluorescent lamp (Philips TLAD 15W/05), which dominantly emits radiation at 365 nm was used. Light intensity ($I = 0.45\ \mathrm{mW\,cm^{-2}}$) was measured using a radiometer type VLX 3W. The lamp and the reactor are on both focal axes of the elliptical chamber. The reaction temperature was kept at 20 ± 1 °C by cycling water. The irradiated solutions and suspensions were magnetically stirred during whole experiments. The suspensions of 2,6-dimethylphenol (5×10^{-4} M) and 1 g L^{-1} of iron oxides were stirred in the dark for 30 min before irradiation to establish adsorption/desorption equilibrium. The particles of iron oxides were removed after irradiation by filtration through cellulose acetate (Millipore 0.45 μm). All solutions were prepared with ultra-pure water (MILIPORE).

2.3. Analytical methods

The disappearance of 2,6-dimethylphenol was monitored by high-performance liquid chromatography using a Shimadzu HPLC equipped with a controller model SCL-10A VP, photodiode-array UV-Vis detector model SPD-M10A VP and two pumps model LC 8A. The system is controlled by software "Class VP5" for storing and processing of chromatograms. The analytical column is a C18 Supelco (5 μm, 250 mm × 4.6 mm i.d). The mobile phase was a mixture of methanol/water (50/50 v/v) was operated at a flow-rate of 1 mL min^{-1}. The detection wavelength was at 270 nm. The UV–Vis absorption spectra were recorded employing a Unicam «Heλios α» spectrophotometer controlled by software "Vision". The ferrous ion can easily be determined by the formation of a red complex with 1,10-phenanthroline. The molar absorption coefficient at 510 nm of the complex Fe (II)-phenanthroline is equal to 11,180 mol^{-1} L cm^{-1} [23]. Hydrogen peroxide was determined using titanium (IV) oxysulfate according to DIN 38402H15.

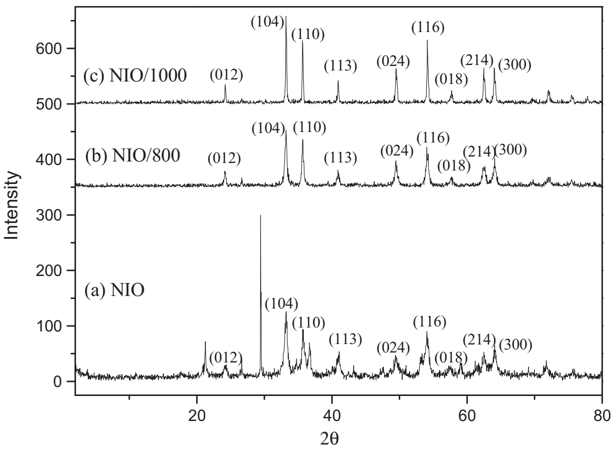

Fig. 1. X-ray powder diffractograms of irons oxides.

2.4. Characterization of irons oxides

To determine the crystal phase composition of natural iron oxide sample and calcined samples at 800 °C and 1000 °C, X-ray diffraction (XRD) measurement was carried out using a spectrometer D8 Advance Bruker NXS, operating at 40 kV and 30 mA, using a Cu K_α monochromatic radiation ($\lambda = 0.15418$ nm). The total surface area and total pore volume of natural iron oxide sample were measured by the Brunauer–Emmett–Teller (BET) method in which the N_2 adsorption at 77 K was applied and (Quantachrome) Sorptometer was used. The natural iron oxide was analyzed by X-ray Fluorescence using CUBIX- PANALYTICAL (Ex PHILIPS) equipment to determine the chemical composition of NIO fractions.

3. Results and discussion

3.1. Properties of iron oxide

The iron oxides samples were examined by XRD to determine their crystals structures. The XRD patterns of natural iron oxide (NIO) as shown in Fig. 1a confirmed that the sample has 9 characteristic peaks of (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (0 1 8), (2 1 4) and (3 0 0), attributable to hematite [24]. It can be seen that the sample has three additional peaks at $2\theta = 21.2$, 29.5 and 36.67. The XRD patterns of calcined natural iron oxide at 800 °C (NIO/800) (Fig. 1b) and 1000 °C (NIO/1000) (Fig. 1c) depict the conversion from mixed crystalline hematite to completely pure crystalline hematite, the three additional peaks were completely disappears. Obviously, the content of hematite increased with the increase of calcination temperature because the relative intensity of (1 0 4) peak for hematite increased with the increase of calcination temperature.