JOURNAL OF ENVIRONMENTAL SCIENCES 43 (2016) 257–264

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JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Relationship between reaction rate constants of organic pollutants and their molecular descriptors during Fenton oxidation and *in situ* formed ferric-oxyhydroxides

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ARTICLE INFO

Article history:
Received 18 August 2015
Revised 15 October 2015
Accepted 15 October 2015
Available online 6 January 2016

Keywords:
Molecular descriptors
Fenton oxidation
Coagulation
Bond order
Fukui indices

ABSTRACT

Fenton oxidation is a promising water treatment method to degrade organic pollutants. In this study, 30 different organic compounds were selected and their reaction rate constants (*k*) were determined for the Fenton oxidation process. Gaussian09 and Material Studio software sets were used to carry out calculations and obtain values of 10 different molecular descriptors for each studied compound. Ferric-oxyhydroxide coagulation experiments were conducted to determine the coagulation percentage. Based upon the adsorption capacity, all of the investigated organic compounds were divided into two groups (Group A and Group B). The percentage adsorption of organic compounds in Group A was less than 15% (wt./wt.) and that in the Group B was higher than 15% (wt./wt.). For Group A, removal of the compounds by oxidation was the dominant process while for Group B, removal by both oxidation and coagulation (as a synergistic process) took place. Results showed that the relationship between the rate constants (*k* values) and the molecular descriptors of Group A was more pronounced than for Group B compounds. For the oxidation-dominated process, E_{HOMO} and Fukui indices ($f(0)_x$, $f(\text{-})_x$, $f(+)_x$) were the most significant factors. The influence of bond order was more significant for the synergistic process of oxidation and coagulation than for the oxidation-dominated process. The influences of all other molecular descriptors on the synergistic process were weaker than on the oxidation-dominated process.

Introduction

Fenton (1894) reported as early as 1894 that ferrous ions strongly promote the oxidation of malic acid by hydrogen peroxide. Subsequent work has shown that the combination of H_2O_2 and a ferrous salt, "Fenton's reagent," is an effective oxidant for a wide variety of organic substrates, such as chlorophenols (Barbeni et al., 1987; Potter and Roth, 1993), chlorobenzene (Sedlak and Andren, 1991), nitrophenols (Kang et al., 1999) and dye pollutants (Kuo, 1992; Solozhenko et al., 1995). Due to its high oxidation potential and fast reaction kinetics, the Fenton reaction has gained much attention for its capability of degrading organics into harmless low molecular weight compounds. Examples of such compounds (degradation products) include carbon dioxide, water and organic acids such as formic acid, acetic and oxalic acid (Muruganandham and Swaminathan, 2004; Sun et al., 2007). The effectiveness of the Fenton process is mainly controlled by the generation of

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http://dx.doi.org/10.1016/j.jes.2015.10.019

hydroxyl radicals, but also can be enhanced by other physico-chemical methods (Pignatello et al., 2006). For instance, Lucas et al. (2007) reported that the decolorization of Reactive Black 5 could reach 91% by a Fenton process enhanced by an aerobic biological treatment. Combination with ultrasound could enhance the decolorization of Acid Orange 7 (Zhang et al., 2009) and improve the COD removal of Reactive Black 8 from aqueous solutions by the Fenton process (Torrades et al., 2004). Yang et al. (2009) presented a microwave-enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater, which removed more than 55% COD and enhanced the 5-day biochemical oxygen demand (BOD5)/COD ratios. Besides these chemical treatments, photo-assisted Fenton-like reactions as a source of hydroxyl radicals have been shown to be effective in the environmental detoxification and photo-degradation of non-biodegradable contaminants, including textile dyes (Herrera et al., 1999; Nadtochenko and Kiwi, 1998; Ruppert et al., 1993; Sawyer et al., 1996).

Based upon our previous research, the choice of appropriate quantum-chemical descriptors is of great importance and can also easily be obtained by computation. Therefore, quantum-chemical descriptors have been applied to develop quantitative structure-activity relationship (QSAR) models to study the relationship between removal and the molecular descriptors of organic pollutants in Fenton oxidation (Jia et al., 2015).

Generally, the Fenton process is composed of the following stages: pH adjustment, oxidation reaction, neutralization, coagulation and solid–liquid separation (Kang and Hwang, 2000). According to Walling and Kato (1971), the basic mechanism of the Fenton process consists of chemical oxidation and coagulation of organic compounds. However, for Fenton precipitation processes, the coagulation step has not yet been completely understood. Therefore, in the present study, focus has been given to the coagulation of ferric-oxyhydroxides formed in the Fenton process. Based upon the adsorption capacity, 30 organic pollutants have been divided into two groups. The relationship between the reaction rate constants (*k*) of the organic pollutants in both groups and their molecular descriptors during Fenton oxidation have been studied. In order to better understand the coagulation of ferric-oxyhydroxides, coagulation experiments for different compounds were conducted. Finally, considering the removal rate constants of the compounds, the effect of the molecular descriptors on the removal rates was discussed.

1. Experiments

1.1. Materials

The 30 organic compounds studied and the hydrogen peroxide solution (30%, *W/W*) were supplied by Alfa Aesar Pty. Ltd., USA. Iron(II) sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) was obtained from Sigma-Aldrich Pty. Ltd., USA. Sodium hydroxide and concentrated sulfuric acid were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All the chemicals were of analytical grade and were used directly without further purification. Water used for chemical solutions was purified by using a Milli-Q® Integral system provided by EMD Millipore Pty. Ltd., USA.

1.2. Fenton oxidation experiments

The initial concentration of highly soluble organic compounds was 100 mg/L. The concentration of the insoluble organic compounds was such that they formed a saturated solution. Fenton oxidation experiments were carried out at room temperature (20 ± 2°C) with a H_2O_2: Fe(II) molar ratio of 10:1. Since the pH of each compound's solution was different, before further treatment pH was adjusted for all solutions to a value of 3.0 by using a 1 mol/L solution of sulfuric acid. While mixing the reaction mixtures, the solutions were stirred continuously using a magnetic stirrer. In each experiment, the ferrous sulfate solution was added to the pH-adjusted solution. H_2O_2 (30%) was added to each solution and the recording of the reaction time was started. 1 mL of 1 mol/L sodium hydroxide solution was added to terminate the reactions at 0.25, 1.0, 2.0, 5.0, 10.0, 20.0, 40.0 and 60.0 min respectively (Pontes et al., 2010). Later, the samples were filtered through 0.45 μm membrane filters to separate the formed precipitates. The concentrations of organic compounds in the supernatant were measured at their maximum absorption wavelengths using a spectrophotometer (HACH DR4000).

1.3. Ferric-oxyhydroxide coagulation experiments

Ferric-oxyhydroxide coagulation experiments were also conducted using the same experimental conditions as were used for the Fenton oxidation experiments. The initial concentration for each organic compound's solution was 100 mg/L, pH was maintained at 3.0 and the temperature was kept constant at 20 ± 2°C. The concentrations of ferrous ion and sodium hydroxide solutions were also the same as for the Fenton oxidation experiments. However, in the coagulation experiments, the H_2O_2 was not added to the reaction systems. Instead, in these experiments, an equivalent dosage of sodium hydroxide was added in order to generate *in situ* flocs of ferric-oxyhydroxides. Later, the samples were filtered through 0.45 μm membrane filters to separate the precipitates formed. The concentrations of organic compounds were determined by using a spectrophotometer (DR4000, HACH Company, USA).

1.4. Computational details

The initial geometries of all the investigated compounds were optimized using density functional theory (DFT) calculations using the DFT/B3LYP model with the 6–311++G(d,p) basis set of the GAUSSIAN09W package (Frisch et al., 2009). The vibrational frequency analysis was done by using HF and B3LYP methods, which also determined the nature of stationary points found by the optimization of geometries. Vibrational frequency analysis revealed that there was no virtual frequency for the optimized structures that would correspond to the minimum points on the potential energy surface. This showed that all of the optimized structures were stable. The energy value for the highest occupied molecular orbital (E_{HOMO}) and that for the lowest unoccupied molecular orbital (E_{LUMO}) was obtained from GAUSSIAN09. The HOMO-LUMO analysis was carried out to explain the charge transfer within the molecule.

Bond order (BO) and Fukui indices ($f(+)$, $f(-)$ and $f(0)$) (Famini et al., 1992; Parr and Yang, 1984) were specifically analyzed by