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Photodegradation of bisphenol AF in montmorillonite dispersions: Kinetics and mechanism study

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ABSTRACT

The photodegradation behavior of bisphenol AF (BPAF) in montmorillonite KSF dispersions was investigated. The influence of KSF dosage, initial BPAF concentration and initial pH on the degradation of BPAF was studied. The main purposes were to clarify the degradation mechanism of BPAF and quantify the fluorine concentration during the degradation. At an initial concentration of 40 μM, more than 78% TOC was removed within 600 min irradiation, and the concentration of fluorine was 0.62 mg L^{-1}. Degradation of BPAF followed the Langmuir–Hinshelwood kinetics rate model and the reaction rate constant k_{re} was 0.887 $\mu M\,min^{-1}$. Hydroxyl radicals were the main reactive species in the irradiated KSF dispersion. Intermediates of BPAF decomposition were determined by LC–MS analysis.

1. Introduction

In recent decades, emerging pollutants in the environment have become a new environmental concern for the scientists and public stakeholders. Emerging pollutants include pharmaceuticals and personal care products (PPCPs), endocrine disrupting compounds (EDCs), surfactants and surfactant metabolites, perfluorinated compounds, sunscreens or UV filters. Recent studies of these compounds have indicated undesired effects at trace concentrations (Gu et al., 2002; Choi et al., 2004; Fent et al., 2006). Unfortunately, existing sewage treatment plants are not well equipped to deal with these compounds (Nakada et al., 2006; Göbel et al., 2007; Gulkowska et al., 2008; Onesios et al., 2009). Analytical technology has allowed for an increasing number of emerging pollutants to be detected in sewage treatment plant (STP) effluents, surface water, ground water, drinking water, sludge, soil and aquatic organisms (Boyd et al., 2003; Dębska et al., 2004; Nikolaou et al., 2007; Soliman et al., 2007; Benotti et al., 2009).

Montmorillonite K series are commercial acid-activated clay minerals that react as solid Brønsted acids. They are mesoporous and have high specific surface areas. Such clay minerals can be used as supports for various transition metal salts and ions. Iron can be a constituent in these clay minerals. Therefore, iron could catalyze Haber–Weiss cycle and promote the generation of reactive radicals through a Fenton-like reaction (Burkitt and Gilbert, 1990; Herney-Ramirez et al., 2008). The hydroxyl radicals and other active oxygen species generated in this processes assist in increasing the photodegradation rate of substances. These supported reagents are widely used in various organic reactions as solid acid catalysts and are becoming novel materials in environmental technology for the removal of harmful substances (Churchman et al., 2006; Liu et al., 2008).

In recent years, the growing interest in the development of new methods for the degradation of toxic pollutants led to the conclusion that the most effective oxidation of organic pollutants is achieved when a powerful oxidizing agent is generated (e.g., $^{\bullet}OH$). These processes are generally called advanced oxidation processes (AOPs). Fenton processes, typical AOPs, were applied to remove bisphenol A (BPA) (Katsumata et al., 2004; Ioan et al., 2007; Liu et al., 2008; Torres et al., 2008; He et al., 2009), which is a representative kind of endocrine disrupter (Chen et al., 2002). Bisphenol AF (BPAF) has a chemical structure similar to BPA and is mainly used as a cross-linking and curing agent in the synthesis of specialty elastomers to improve their chemical and thermal properties. However, the introduction of fluorine increased the degradation resistance (Khetan and Collins, 2007). In our previous work (Liu et al., 2008), we investigated the degradation of BPA in KSF dispersions and BPA was effectively removed during the degradation. Fluorine, generated during the BPAF degradation, can also be a pollutant. It has been reported that montmorillonites demonstrated high performance in removing fluorine from aqueous solution (Agarwal et al., 2002; Tor, 2006). Therefore, we investigated the degradation of BPAF in montmorillonite KSF dispersions.

2. Materials and methods

2.1. Reagents

BPAF (97%) was purchased from Aldrich and was used as received. Methanol was spectroscopic grade (Fisher). Montmorillonite KSF was purchased from Sigma-Aldrich. The major chemical components of

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KSF were determined on Philips PW1480 X-ray fluorescence (XRF) spectrometer (Table 1). Iron oxide and free iron were removed by citrate–dithionite (Mehra and Jackson, 1958). After this reaction, only structural iron remains (Table 1). Citrate–dithionite reacted KSF was used to check the role of structural iron in the BPAF degradation. Isopropanol (IPA, 99.5+%, Aldrich) was used as the hydroxyl radical scavenger. $HClO_4$ and NaOH aqueous solutions were used to adjust pH. Ultrapure water (18.2 MΩ cm) was used throughout the experiments.

2.2. Photodegradation

In the photodegradation experiments, a metal halide lamp ($\lambda \geq 365$ nm, 250 W) (Wang et al., 2006) and a XPA photochemical reactor equipped with a water-cooling system (Nanjing Xujiang Electromechanical Company, China) were used. The KSF dispersions in the 500 mL photoreactor were vigorously stirred with a magnetic stirrer throughout the photochemical experiments. The KSF dispersion was equilibrated with BPAF in the dark for an hour before irradiation. After this period, 2 mL aliquots were withdrawn to determine the concentration C_0. During all the oxidation reactions, 2 mL aliquots were withdrawn at selected time intervals, centrifuged and used for concentration determination. Degradation efficiency of BPAF at different times was defined as $E = \frac{c_0 - c_t}{c_0} \times 100$. The initial rate of BPAF photodegradation R_0 (μM min^{-1}) was determined by extrapolating the tangent (based on the linear fit of the points) of the concentration profile back to initial conditions.

2.3. Analysis

The concentration of BPAF was determined by HPLC [DIONEX P680, Kromasil 100-5C18 column (4.6×250 mm, 5 μm)] with a flow rate of 1.0 mL min^{-1} and UV absorbance detection at 280 nm. The mobile phase was a CH_3OH/H_2O mixture (75/25, v/v). The injection volume was 20 μL.

The generated fluorine ions during the degradation were quantified by ion chromatography (IC; DX500, Dionex). The total organic carbon (TOC) of the solution was measured with a Shimadzu TOC-5000A instrument.

Liquid chromatography mass spectrometry (LC–MS) was carried out on the Agilent 1100 setup. Mass spectrometry was performed with electrospray ionization (ESI) in negative mode. The column was a ZORBAX SB-C18 column (4.6×250 mm, 5 μm) at 40 °C. The eluate was introduced into the electrospray interface (temperature, 250 °C; needle kV, 1.97 kV). The elution was carried out at a rate of 200 μL min^{-1} with an aqueous solution of acetonitrile/10 mM ammonium acetate (4:6, v/v).

3. Results and discussion

3.1. Control experiments

The concentration of BPAF in the absence of KSF under direct photolysis or in darkness in the presence of KSF hardly changed and BPAF degradation was <5% during 120 min (Fig. 1). Thus, direct photolysis had less influence on the BPAF degradation due to a small overlapping of the lamp emission spectrum with the BPAF absorption spectrum.

Table 1
Major chemical components of KSF and citrate–dithionite reacted KSF determined by X-ray fluorescence analysis (mass%).

	SiO_2	Al_2O_3	SO_3	Fe_2O_3	MgO	CaO	K_2O	TiO_2	Na_2O
KSF	49.1	16.3	22.3	4.76	4.31	2.3	0.495	0.21	0.057
Citrate–dithionite reacted KSF	71.2	17.7	0.338	4.15	2.81	0.0778	0.532	0.244	2.78

After 120 min of irradiation in the presence of KSF, almost 98% of BPAF was decomposed. Degradation was mainly caused by the hydroxyl radical resulting from the photolysis of $Fe(OH)^{2+}_{aq}$ complexes. KSF contains both free iron and structural iron. To better clarify the contribution of free iron (homogeneous pathway) and structural iron (heterogeneous pathway) the photodegradation of BPAF in the filtrate of the montmorillonite KSF was compared with that of citrate-dithionite reacted KSF. The solid KSF was separated by filtration using 0.22 μm filters before irradiation. The result clearly showed that the efficiency of the heterogeneous pathway of photodegradation was much smaller than that of the homogeneous reaction.

Purging the dispersion with N_2 instead of air, suppressed the decomposition of BPAF and degradation was limited to 42%, which revealed dissolved oxygen was a large influence on the degradation. As observed in many studies (Sun and Pignatello, 1993; Nedoloujko and Kiwi, 1997; Utset et al., 2000; Rodriguez et al., 2003; Aris and sharratt, 2006; Du et al., 2007) the efficiency of Fenton-like systems was higher in the presence of O_2 when compared with other gases such as helium, argon or nitrogen. Degradation process in the Fenton systems were likely promoted by the reaction of O_2 with intermediate organoradicals. In the heterogeneous pathway, towards the end of the hydroxyl radical formation, oxygen increased the rate of decay and formed superoxide anion radicals through the oxygen dependent reaction with iron.

$$O_2 + Fe^{2+} + h\nu \rightarrow Fe^{3+} + O_2^{-\bullet} \tag{1}$$

$$\text{Structural} - Fe(II)[\text{claymineral surface}] + O_2 + h\nu \rightarrow \text{Structural} - Fe(III) + O_2^{-\bullet} \tag{2}$$

$$2O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet \tag{3}$$

$$HO_2^\bullet/O_2-^\bullet + Fe^{2+} \rightarrow H_2O_2 + Fe^{3+} \tag{4}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \tag{5}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH. \tag{6}$$

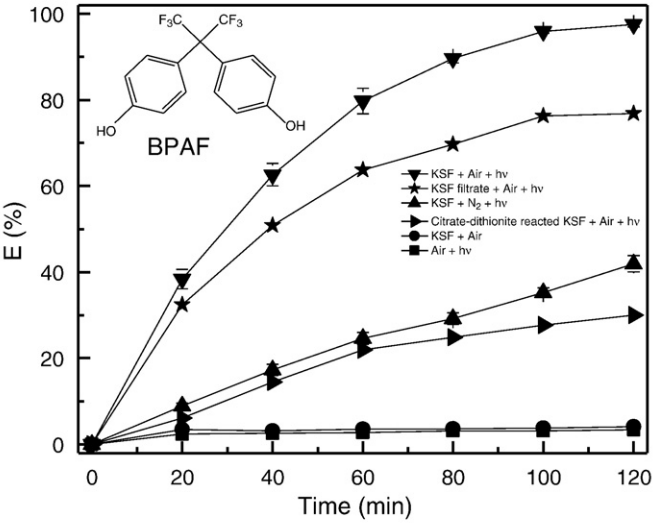

Fig. 1. Photodegradation of BPAF. BPAF initial concentration 40 μM, montmorillonite content = 1.0 g L^{-1}, pH = 3.7.