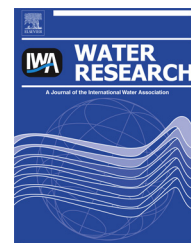


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Catalytic effect of transition metals on microwave-induced degradation of atrazine in mineral micropores

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ARTICLE INFO

Article history:

Received 12 December 2013

Received in revised form

3 March 2014

Accepted 7 March 2014

Available online 18 March 2014

Keywords:

Microporous minerals

Microwave-induced degradation

Catalytic effect

Transition metals

Atrazine

ABSTRACT

With their high catalytic activity for redox reactions, transition metal ions (Cu^{2+} and Fe^{3+}) were exchanged into the micropores of dealuminated Y zeolites to prepare effective microporous mineral sorbents for sorption and microwave-induced degradation of atrazine. Due to its ability to complex with atrazine, loading of copper greatly increased the sorption of atrazine. Atrazine sorption on iron-exchanged zeolites was also significantly enhanced, which was attributed to the hydrolysis of Fe^{3+} polycations in mineral micropores and electrostatic interactions of protonated atrazine molecules with the negatively charged pore wall surface. Copper and iron species in the micropores also significantly accelerated degradation of the sorbed atrazine (and its degradation intermediates) under microwave irradiation. The catalytic effect was attributed to the easy reducibility and high oxidation activity of Cu^{2+} and Fe^{3+} species stabilized in the micropores of the zeolites. It was postulated that the surface species of transition metals (monomeric Cu^{2+} , Cu^{2+} -O-Cu²⁺ complexes, FeO^+ , and dinuclear Fe-O-Fe-like species) in the mineral micropores were thermally activated under microwave irradiation, and subsequently formed highly reactive sites catalyzing oxidative degradation of atrazine. The transition metal-exchanged zeolites, particularly the iron-exchanged ones, were relatively stable when leached under acidic conditions, which suggests that they are reusable in sorption and microwave-induced degradation. These findings offer valuable insights on designing of effective mineral sorbents that can selectively uptake atrazine from aqueous solutions and catalyze its degradation under microwave irradiation.

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1. Introduction

We have been working on the development of a novel treatment technology that removes organic contaminants from water using microporous mineral sorbents and then induces the degradation of the contaminants sorbed in mineral micropores (<2 nm) with microwave irradiation (Hu et al., 2012; Hu and Cheng, 2013a,b). One of the most effective and affordable agricultural herbicides, atrazine, which was frequently detected in surface water and groundwater at concentrations up to the $\mu\text{g/L}$ level in Europe and North America (Giddings et al., 2005; Loos et al., 2010), was selected as the target contaminant. Because conventional drinking water treatment processes are ineffective at their removal, there has been significant attention on the development of viable technologies for removing atrazine and other pesticides (Benner et al., 2013). Our study showed that atrazine could be effectively sorbed on dealuminated Y zeolites due to the combination of molecular-dimension pores and the relatively hydrophobic pore wall surfaces (Hu et al., 2012; Hu and Cheng, 2013a). Furthermore, the framework of Y zeolites is transparent to microwave, allowing the microwave energy to act almost exclusively on the polar species in the micropores, namely, sorbed atrazine, sorbed water, and cations (Hu et al., 2012; Hu and Cheng, 2013a). Microwave radiation did not directly cause degradation of the atrazine sorbed in mineral micropores, as its energy (0.98 J/mol at 2.450 GHz) is far below those of common chemical bonds in organic molecules (hundreds of kJ/mol) (Vladimir and Stanislav, 2011). Instead, atrazine molecules degraded via pyrolysis caused by the micro-scale “hot spots” formed in the micropores due to the interfacial selective heating of microwave (Conner and Tompsett, 2008; Hu et al., 2012; Hu and Cheng, 2013a). The rate of microwave-induced degradation has been observed to be influenced by the type and density of surface cations, as well as the amount of water present in the micropores (Hu and Cheng, 2013a). Further optimization of the mineral sorbents by incorporating catalytic species is expected to make this process more cost-effective in the practical applications of treating surface water contaminated by atrazine and other nitrogen-containing herbicides.

The chemical properties of zeolites, including density of acidic sites (determined by the framework Si/Al ratio), and the type and amount of metal ions and metal oxides doped in zeolite cages and channels are well known to affect their catalytic performance (Lone et al., 1984; Lukyanov, 1992; Zaidi and Pant, 2004, 2005). Zeolites modified with Cu^{2+} and Fe^{3+} have high catalytic activity for a range of oxidation reactions, such as oxidation of methane, propane, and benzene, and oxydehydrogenation of ethane (Chang et al., 1995; Nowinska et al., 2003; Ryder et al., 2003; Smeets et al., 2005). Transition metals exchanged into the cages and channels of zeolites can function as highly active sites for many catalytic reactions. Depending on the conditions of ion exchange and the amount of metal ions exchanged, the metals can be present in the forms of isolated cations (Me^{n+}) and/or metallic species, such as $(\text{Me}-\text{O}-\text{Me})^{(2n-2)+}$ oxocations and $(\text{MeO})^{(n-2)+}$ cations, where n is the metal valence (Urquieta-Gonzalez et al., 2002). In addition, extra-framework metallic oxides may also be

deposited in crystalline and/or amorphous forms on the internal and external surfaces of the zeolites (Gervasini, 1999). Although there is no general consensus on the nature of the active sites or the mechanism for transition metals in redox catalysis, their reversible reduction and re-oxidation is believed to be key to the catalytic activity. On copper-exchanged zeolites, the active site responsible for the high catalytic activity has been attributed to the unique dimeric Cu species (e.g., $\text{Cu}^{2+}-\text{O}^{2-}-\text{Cu}^{2+}$, $\text{Cu}^{+}-\text{O}^{2-}-\text{Cu}^{2+}$, and $\text{Cu}^{+}\bullet\bullet\text{Cu}^{2+}-\text{O}-$) stabilized by the zeolite framework (Campa et al., 1994; Moretti, 1994; Moretti et al., 1999), while monomeric Cu^{2+} has also been proposed to be the catalytic center (Larsen et al., 1994; Konduru and Chuang, 1999; Wichterlova et al., 1995).

This study was conducted to harness the catalytic property of transition metals in redox reactions to develop effective mineral sorbents for microwave-induced degradation of atrazine. The results showed that the loading of transition metals copper and iron greatly increased the atrazine sorption capacity of dealuminated Y zeolites. Furthermore, compared to the ions of alkali and alkaline-earth metals, the surface species of transition metals exchanged into the mineral micropores accelerated the microwave-induced degradation of the sorbed organic contaminants through serving as catalytic sites, and thus allowing the microwave energy to be utilized more efficiently. The active surface species of the transition metals in the mineral micropores, i.e., monomeric Cu^{2+} , $\text{Cu}^{2+}-\text{O}-\text{Cu}^{2+}$ complexes, FeO^{+} , and dinuclear $\text{Fe}-\text{O}-\text{Fe}$ -like species, were identified with the aids of diffuse reflectance infrared Fourier transform (DRIFT) and ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) spectrad. The mechanism of transition metal ions in microwave-induced degradation in mineral micropores, which involves thermal activation under microwave irradiation and generation of highly reactive species with the reversible $\text{Me}^{n+}-\text{Me}^{(n-1)+}$ change, was also proposed for the first time. The pathways and kinetics of microwave-induced atrazine degradation catalyzed by copper and iron species in mineral micropores were also delineated, which can help establish the conditions necessary for complete mineralization. The copper and iron on the metal-exchanged zeolites were found to have good stability under acidic conditions, indicating such zeolites, particularly the iron-exchanged ones, could be reusable for sorption and microwave-induced degradation. These transition metal-exchanged microporous mineral sorbents show great promises in practical application of the microwave-based contaminant removal and destruction technology.

2. Materials and methods

2.1. Chemicals

Atrazine (98.4%), hydroxyatrazine (99.0%), deethylatrazine (98.0%), N-ethyl-ammeline (99.5%), and ammeline (98.0%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Deisopropylatrazine (98.0%) and N-isopropyl-ammeline (95.0%) were supplied by AccuStandard (New Haven, CT). HPLC grade methanol was obtained from CNW Technologies (Dusseldorf, Germany). Instrument calibration standards were prepared in

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