Research article

Removal of antibiotic sulfamethoxazole by zero-valent iron under oxic and anoxic conditions: Removal mechanisms in acidic, neutral and alkaline solutions

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ABSTRACT

Removal of antibiotic sulfamethoxazole (SMX) by zero-valent iron (ZVI) was examined in the range of pH from 3.0 to 11.0 under oxic and anoxic conditions to clarify mechanisms of SMX removal in acidic, neutral and alkaline solutions. SMX removal was affected by solution pH and related to the speciation of SMX. Under the oxic condition, the maximums of SMX removal efficiency and rate were obtained at pH 3.0. The SMX removal efficiency decreased from 100 to 32% with increasing pH in the acidic solutions ($3 \leqq pH \leqq 5$) and increased to 88% in neutral and moderately alkaline solutions ($6 \leqq pH \leqq 10$). In highly alkaline solution ($pH = 11$), the SMX removal was significantly suppressed due to the formation of passive layer on ZVI surface. The removal rate of SMX under the oxic condition significantly declined with increasing pH. Under the anoxic condition, SMX removal was completed within 300 min in the acidic solutions and remained to less than 70% after 300 min in neutral and moderately alkaline solutions. For $pH \geqq 10$, no SMX removal practically occurred. The removal rate of SMX under the anoxic condition approximately remained constant in the acidic solution and largely decreased in neutral and moderately alkaline solutions. SMX removal by ZVI was found to be dominated by the reductive degradation and adsorption under both the oxic and anoxic conditions. It was concluded that ZVI has the potential for effective removal of antibiotic SMX under the oxic and anoxic conditions. A kinetic model could reasonably simulate the dynamic profiles of SMX removal.

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1. Introduction

A variety of antibiotics have been discharged from medical, municipal and agricultural sources due to excessive dosage and disposal of unused antibiotics. Therefore, the removal of antibiotics in the aquatic environment is one of the emerging environmental issues (Yu et al., 2016; Michael et al., 2013; Rivera-Utrilla et al., 2013; Homem and Santos, 2011). In general, biological treatment processes have been ineffective in the removal of antibiotics (Michael et al., 2013). Sulfamethoxazole (SMX) being a sulphonamide type synthetic antibiotic has been used for treatment of bronchitis and urinary tract infections and often found at higher concentrations in environmental water as compared with other

sulphonamides (Zhang et al., 2016). Since SMX having low biodegradability persists in the environment for more than one year (Gonzalez et al., 2009), effective advanced treatment processes are required to prevent antibiotics entering the natural environment.

Recently, zero-valent iron (ZVI) technology has received growing attention as a highly efficient water treatment (Zhao et al., 2016; Sun et al., 2016; Raman and Kanmani, 2016). ZVI having reductive and adsorptive capabilities is an excellent agent for chemically reducing various pollutants such as organic compounds, heavy metals, pesticides and inorganic anions. The adsorptive capability and reductive activity towards an extensive range of contaminants along with its cheap and wide accessibility made ZVI as a versatile material for removal of contaminants in water. Ghauch et al. (2013) and Ayoub and Ghauch (2014) have applied ZVI technology to degradation of SMX. However, the practical application of ZVI process is limited due to a lack of quantitative information for mechanisms of pollutant removal by ZVI. For rational design and operation of ZVI processes for SMX removal,

knowledges of removal mechanisms and reaction kinetics are required. The removal of organic pollutants by ZVI is attributed to four mechanisms, i.e. reductive degradation, oxidative degradation, coagulation/sedimentation and adsorption (Fu et al., 2014; Sun et al., 2015). The Fe elution and the formation of iron oxide/hydroxide layer on ZVI surface controlling the four removal mechanisms are strongly affected by solution pH. However, very little quantitative information on the contribution of iron oxide/hydroxide layer formed on the ZVI surface to the removal of organic pollutants is available in literature. The aim of this study is to clarify effects of solution pH on mechanisms for SMX removal using ZVI under the oxic and anoxic conditions. To achieve this goal, the SMX removal process was simulated using a reaction kinetic model proposed newly by considering the change in speciation of SMX with pH. To obtain an insight for the formation of iron oxides/hydroxides on ZVI surface, the surfaces of ZVI particulates before and after reaction were characterized by X-ray diffraction and scanning electron microscopy with an energy dispersive spectroscopy.

2. Materials and methods

2.1. Materials

Sulfamethoxazole (SMX) was purchased from Sigma-Aldrich Japan Co. (Tokyo, Japan). Potassium dihydrogen phosphate and acetonitrile used in HPLC analysis were purchased from Kanto Chemical Co. (Japan). Reagent grade sulfuric acid and sodium hydroxide used to control solution pH were purchased from Kanto Chemical Co. (Japan). All reagents were used as received.

ZVI particulates with the average diameter of 215 μm were purchased from Kanto Chemical Co. (Japan). The specific surface area of ZVI determined by the BET-N$_2$ method was 0.31 m^2 g^{-1}.

2.2. Characterization

The characterization of ZVI surface was carried out after 300 min reaction when as shown below total organic carbon (TOC) removal had approximately reached the steady-state. X-ray diffraction spectroscopy (XRD) data were obtained for confirming the material composition in passive layer formed on ZVI surface by Bruker AXS D8 ADVANCE ECO (Bruker, Germany) using Cu Kα radiation at 40 kV/25 mA. Data were collected in the 2θ range from 20° to 90°. The morphology of the resulting ZVI particulates was determined using a field emission scanning electron microscope (SEM) (FE-SEM SU8030, Hitachi Ltd., Japan) with an energy dispersive X-ray spectroscope (EDS) (EDS EX-250, Horiba Ltd., Japan).

2.3. Removal of SMX

Experiments were carried out in a Pyrex glass cylindrical reactor of 1.0 L working volume and conducted in a batch mode. SMX of 32 mg was dissolved in a 1L of ultrapure water (Arium pro UV-DI, Sartorius Stedim Biotech GmbH, Japan). Although this initial SMX concentration is considerably larger than the typical concentration in the aquatic environment (from ng L^{-1} to μg L^{-1} levels) (Kummerer, 2009), it was chosen for highly accurate determination of SMX concentration by the HPLC (Xekoukoulotakis et al., 2011; Ji et al., 2014). The HPLC (UV-2075Plus, JASCO Co., Japan) with a 5 μm particle size Inertsil ODS-3V column (GL Science Co., Japan) was used to determine the concentrations of SMX (Shimizu et al., 2012). The solvent used was the mixture of acetonitrile and potassium dihydrogen phosphate solution at the ratio of 65/35 (v/v). The extent of SMX mineralization was determined as a decrease in TOC dissolved in the solution using a TOC meter (TOC-VE, Shimadzu Co., Japan).

The solution pH was regulated to the specified pH either by adding H$_2$SO$_4$ or NaOH using the pH controller (NPH-680D, Nisshin-Rika Co., Japan). The concentrations of total Fe ion and ferrous ion were determined by the 1,10-phenanthroline method (Shimizu et al., 2012). It should be noted that the total iron ions mostly consisted of Fe^{2+}. To conduct the experiments under the oxic and anoxic conditions, during the experiments air or nitrogen gas was continuously injected in the solution at the flow rate of 0.5 L min^{-1} through a sintered glass cylinder sparger installed near the reactor base to saturate the solution with oxygen or to purge dissolved oxygen (DO), respectively. The DO concentration was measured using a DO meter (Seven2Go, Mettler Toledo International, Japan).

The experiments started by adding ZVI of 3.0 g. At predetermined time intervals samples from the liquid phase were withdrawn using a syringe. To remove ZVI particles, the liquid samples were filtered with 45 μm syringe filters. Most of the experiments were conducted in duplicate or triplicate to assure accurate data and the maximum deviation was found to be approximately 15%. All results presented are the average values of duplicate or triplicate experimental results.

3. Results and discussion

3.1. Characterization

Fig. 1 depicts the XRD patterns, SEM images and EDS analyses of ZVI before and after reaction for 300 min at different solution pH values under the oxic and anoxic conditions. EDS measurements were carried out to confirm changes in the presence of elements on the ZVI surface.

The characterization of ZVI before reaction was conducted for reference. It is seen in Fig. 1a that before reaction only the peaks for Fe^0 at 44°, 65° and 82° were found and no iron oxide/hydroxide peaks were practically detected in the XRD analysis. The SEM image showed a rather smooth surface despite a little of uneven surfaces. EDS analysis resulted in that elements of ZVI before reaction were composed of C (6.22 wt %), O (1.36 wt %) and Fe (92.42 wt %).

In Fig. 1b, XRD patterns, SEM images and EDS analyses of ZVI after reaction under the oxic condition are shown. The XRD pattern for characterization of ZVI after reaction of 300 min at pH 3.0 reveals that several peaks of iron oxides/hydroxides such as FeOOH, Fe$_2$O$_3$ and Fe$_3$O$_4$ were detected. This suggests that significant corrosion of ZVI and formation of iron oxides/hydroxides vigorously took place at pH 3.0 under the oxic condition.

By ZVI corrosion, the electrons are emitted and Fe^{2+} and Fe^{3+} are generated:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{2}$$
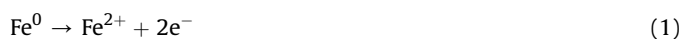
The oxidation of Fe^0 into Fe^{2+} and subsequently into Fe^{3+} proceeds to the formation of iron oxides/hydroxides.

Under the oxic condition, iron corrosion generates hydrogen peroxide (Fu et al., 2014).

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{3}$$
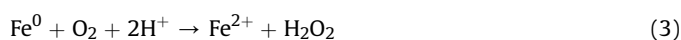
Subsequently, H$_2$O$_2$ reacts with Fe^{2+} and produces highly reactive hydroxyl radical.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \quad \text{(Fenton reaction)} \tag{4}$$

As described below, the oxidative degradation of organic pollutants