Degradation of pyrene in cetylpyridinium chloride-aided soil washing wastewater by pyrite Fenton reaction

CrossMark

Kyunghoon Choi, Sungjun Bae, Woojin Lee *

Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

HIGHLIGHTS

- Both pyrene and CPC were effectively degraded in 180 min by pyrite Fenton reaction.
- Iron was dissolved continuously and reacted with H_2O_2 to produce $OH\cdot$.
- CPC was degraded to CO_2 and ammonium as main degradation products.
- No oxy-pyrenes were accumulated during pyrene degradation in pyrite Fenton system.

ARTICLE INFO

ABSTRACT

Degradation of pyrene by pyrite Fenton reaction in synthetic cetylpyridinium chloride (CPC)-aided soil washing wastewater (SWW) was investigated in a closed batch reactor. Pyrene in the presence of CPC was gradually degraded in the pyrite Fenton system by 96% in 180 min at initial pH 7 showing pseudo-first-order reaction kinetics ($0.0194\ min^{-1}$), while the concentration of pyrene in the absence of CPC decreased abruptly by 91% in 5 min and then did not significantly decrease by the end of sampling time (180 min). In a classic Fenton system, pyrene in the presence of CPC was degraded by 35% in 180 min at initial pH 3. The sustainable reactivity of pyrite Fenton was attributed to slow but continuous dissolution of Fe(II) from the pyrite surface leading to continuous production of reactive radicals during the reaction. Pyrene in the presence of CPC was mainly degraded by OH radicals. Its product study showed that the pyrite Fenton system can successfully degrade pyrene in the CPC-aided SWW without accumulating toxic oxy-pyrenes such as 1,6-pyrenequinone and 1,8-pyrenequinone. CPC was also successfully degraded (95%) in the pyrite Fenton system, forming carbon dioxide and ammonium as main degradation products.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are representative environmental aromatic contaminants composed of two or more fused aromatic rings. PAHs can be produced naturally by the incomplete combustion of organic compounds during forest fires and volcanic eruptions, but mostly come from anthropogenic sources, i.e., vehicle exhaust and incineration facilities using fossil fuels, oil spillage, and even cigarette smoking [1]. They are ubiquitous pollutants present in soil, sediment, water and atmosphere and are harmful to plants and animals due to their mutagenicity and carcinogenicity [2]. In addition, low bioavailability of PAHs due to their high hydrophobicity [3] led to the application of surfactants to most of soils contaminated with PAHs (i.e., surfactant-aided soil washing), which usually can enhance the solubility of PAHs by decreasing the interfacial tension and increasing their partitioning to the hydrophobic cores of surfactant micelles [4]. This process can simply and efficiently treat the contaminated soils. However, it can produce surfactant-aided soil washing wastewater (SWW) additionally during the process. SWW cannot be easily treated by conventional wastewater treatments due to recalcitrant PAHs combined with large surfactant molecules composed of complex organic groups [5]. Based on the guideline of soil washing by the United States Environmental Protection Agency, the SWW should be disposed of in accordance with a National Pollution Discharge Elimination System permit [6] requiring its treatment at on-site or in public wastewater treatment plants (WWTPs). However, no significant monitoring data on treatment of SWW in WWTPs are available and even no discharge requirement of PAHs in final WWTP effluent has been set to date. Concentrations of PAHs at contaminated sites have been reported in the range of

1 μg/kg to 775 mg/kg, however those in the SWW have not been properly informed yet [7,8].

PAHs and surfactants present in SWW have been treated conventionally by activated carbon adsorption and ultra-filtration processes to separate spent surfactants from the contaminants [9,10]. To treat and reuse SWW including PAHs and surfactants, ozone [11], photochemical treatment [12–16], Fenton [17–19], electro-Fenton [5], and photo-Fenton [20] processes have been adopted as well. Among the processes for the treatment of PAHs and surfactants, the adsorption process showed low selective adsorption removal for PAHs (∼55%) resulting in generation of toxic wastes containing PAHs. Ultra-filtration process also needs to treat the similar toxic wastes further. The photochemical process (UV/H_2O_2) with recalcitrant surfactant (lithium perfluorooctanesulfonate resistant to oxidants) seems to be difficult due to the limited use of specific surfactant. Moreover, the photochemical stability of the surfactant was not clearly known. Studies for AOPs treating PAHs in SWW have mostly focused on the degradation of target chemicals but not significantly on the effect of surfactant in the SWW. Removals of PAHs by ozone and photo-catalyst have been commonly known to be lower than those by Fenton process [21,22]. Recently, classic Fenton system has shown to effectively degrade p-cresol at neutral pH without significant loss of nonionic surfactant [19]. However, most classic Fenton systems need proper control of operating conditions such as suspension pH during the treatment of contaminated soil, which is a challenging problem that needs to be overcome [23,24]. In addition, classic Fenton system has been known that its reaction frequently formed toxic transformation products. Lee et al. and Lee and Hosomi reported that anthracene and benzo[a]anthracene were degraded by the Fenton reaction by 97% and each target substance was further transformed to oxy-PAHs by 68% and 39%, respectively [17,25]. The oxygenated PAHs have been known to be more persistent than the targets [26] and some of them have been reported not to be degraded any further by the Fenton reaction [18]. Heterogeneous Fenton-like processes have been developed to solve such complex issues. Pyrite Fenton system has successfully removed recalcitrant organic substances including chlorinated organics (carbon tetrachloride (CT) and trichloroethylene (TCE)), explosives (2,4,6-trinitrotoluene), and pharmaceutical (diclofenac) in contaminated soil suspensions [27–30]. However, no research has properly investigated the degradation of both PAH and surfactant in SWW by the heterogeneous Fenton reaction and identified its complex reaction mechanism yet. Moreover, no significant study has been carried out to fully identify distribution of transformation products such as oxy-PAHs during the reaction to date.

In this research, we investigated the suitability of a novel pyrite Fenton system for the oxidative degradation of PAH in synthetic surfactant-aided SWW and elucidated its major transformation products and degradation mechanism during the reaction. We selected pyrene, four fused-benzene ring PAH, as a representative PAH because it is mutagenic and persistent in diverse environments and ubiquitously found in contaminated soils [14]. Cetylpyridinium chloride (CPC), one of cationic surfactants, was selected as a model surfactant because it is hardly biodegraded and more detrimental to plants and animals than any other surfactants [31].

2. Experimental section

2.1. Reagents

Chemicals used in this study were CPC (>99.0%, Sigma), pyrene (98%, Aldrich), ferrous sulfate heptahydrate (FeSO$_4$·7H$_2$O, 99%, Sigma), and hydrogen peroxide (30 wt.%, Junsei). Nitric acid (60%, Junsei) was used for removal of oxidized surface layer on pyrite.

Sodium hydroxide (97%, Sigma) and sulfuric acid (99.999%, Aldrich) was used to adjust initial suspension pHs of batch samples. Tert-butanol (t-butanol, >99%, Sigma) and chloroform (99.9%, Sigma–Aldrich) were used as OH· and superoxide (O_2^-) scavengers for inhibition experiments. Acetonitrile (99.9%, J.T. Baker) as an eluent of high-performance liquid chromatograph (HPLC) for the analysis of pyrene, methanol (99.9%, Merck) for the preparation of stock solutions and samples, and ethanol (95%, Jin Chemical) for pyrite pretreatment were all HPLC grade. Acetone (99.9%, Merck), acetonitrile (described above), and dichloromethane (DCM, 99.9%, Merck) for the extraction of pyrene (gas chromatograph/mass spectrometer (GC/MS)) and the preparation of stock solution of pyrene and its transformation products were also all HPLC grade. For pyrene transformation products study, 1-hydroxypyrene (1-HP, 98%, Aldrich), acetic anhydride (⩾98%, Sigma–Aldrich), sodium dichromate dehydrate (⩾99.5%, Sigma–Aldrich), basic alumina (0.063–0.200 mm, Merck), diisooctyl ester 1,2-benzenedicarboxylic acid (diisooctyl phthalate (DIOP), ⩾99%, Aldrich), phthalic acid dibutyl ester (dibutyl phthalate, 99%, Aldrich), 1,2-benzenedicarboxylic acid (phthalic acid, 99.5%, Sigma–Aldrich), stearic acid (⩾98.5%, Sigma), palmitic acid (PA, ⩾99%, Sigma), tricosane (99%, Aldrich), and hexadecane (HD, 99%, Sigma–Aldrich) were purchased and used without further purification. Pyrene degradation products (1,6-pyrenequinone (1,6-PQ) and 1,8-pyrenequinone (1,8-PQ)) were synthesized based on the method by Cho and Harvey [32]. For the analysis of CPC, orange G (Sigma), sodium acetate trihydrate (99%, Sigma–Aldrich), acetic acid (99.7%, Junsei) and chloroform (described above) were used. Distilled water was purified using an ultrapure filtration system (ELGA PURELAB Classic system) to obtain 18 MΩ cm pure deionized water (DIW). It was used for characterization tests as controls and for preparation of all solutions and suspensions.

Pyrite (FeS$_2$, Zacatecas, Mexico) was purchased from Ward's Natural Science, and ground using a ceramic mortar and pestle. The smashed particles were passed through a 150 μm sieve, ultra-sonicated in ethanol for 5 min to remove fine particles, and washed with 1 M nitric acid to eliminate oxidized surfaces. The pyrite sample was rinsed with DIW and then with ethanol to dehydrate the surface and finally dried and stored in a closed glass vial, which was placed in an anaerobic chamber until being used. Prepared pyrite was analyzed by X-ray diffraction (XRD) to investigate its purity and identity. It showed a good agreement with those in Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data files (JADE 9, Materials Data, Inc.) (data not shown). Unless stated otherwise, all experiments were conducted with following experimental conditions: 25 mM Fe(II) (i.e., pyrite and soluble Fe(II)), 42.03 μM pyrene with CPC, 0.213 μM pyrene without CPC, 1.8 mM CPC, 9.8 mM H$_2$O$_2$, initial pH 7 for pyrite Fenton system, and initial pH 3 for classic Fenton system.

2.2. Experimental procedures

Batch kinetic experiments were conducted at room temperature (25 ± 0.5 °C) under aerobic condition for the characterization of pyrene degradation with and without CPC by pyrite Fenton reaction using an amber borosilicate glass vial (nominal volume: 20 mL, Kimble) with open-top cap applying a three layered septum system [33]. CPC solution (1.8 mM) was prepared by dissolving an exact amount of CPC (0.6444 g) in 1 L of DIW in an Erlenmeyer flask. The CPC solution was adjusted to initial pH 7 using NaOH (0.4 M). Pyrene solutions were prepared by adding an exact amount of crystalline pyrene (0.0101 g) to DIW or CPC solution in a flask wrapped with aluminum foil to avoid photo-degradation and by mixing it by a magnetic stirrer for 48 h. The solutions were filtered through a medium porosity-fritted glass funnel to remove any microcrystalline pyrene. They were used as synthetic