Chemosphere 141 (2015) 205–211

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

An integrated biodegradation and nano-oxidation used for the remediation of naphthalene from aqueous solution

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HIGHLIGHTS

- Naphthalene remediation integrates biodegradation and Fenton-like oxidation.
- Removal of COD increased from 36.4% to 91.6% by Fe nanoparticles.
- Naphthalene transformation products were completely mineralized.
- This method has great potential for naphthalene remediation.

ARTICLE INFO

Article history:
Received 29 January 2015
Received in revised form 11 June 2015
Accepted 18 July 2015

Keywords:
Biodegradation
Naphthalene
Fenton-like oxidation
Hydroxyl radical
nZVI

ABSTRACT

The remediation of toxic persistent organic contaminants in the environment has raised a need for effective cleanup methods. In this study, an integrated remediation technique based on biodegradation of naphthalene using *Bacillus fusiformis* and Fenton oxidation of their degraded metabolites using nanoscale zero-valent iron (nZVI). A 99.0% naphthalene was biodegraded by *B. fusiformis* in 96 h, while only 59.4% chemical oxygen demand (COD) was removed, indicating that the degraded metabolites existed in solution. To further degrade the metabolites, nanoscale zero-valent iron (nZVI) was used as heterogeneous catalyst for Fenton-like oxidation of the metabolites after biodegradation lasting 40 h. Results showed that the total the removal COD increased from 36.4% to 91.6% at pH 3.0, 1.0 g L^{-1} nZVI, 10.0 mM L^{-1} H_2O_2 and temperature of 35 °C. Scanning electron microscopy (SEM) showed the aggregation and corrosion of nZVI. X-ray diffraction (XRD) confirmed the existence of Fe^0 and the presence of iron oxide (Fe(II)) and iron oxohydroxide (Fe(III)). A possible degradation pathway was proposed since two naphthalene metabolites (1-Naphthalenol and 1,4-Naphthalenedione) were detected by GC–MS.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a large group of aromatic hydrocarbons with two or more fused benzene rings, which are discharged into the environment from natural as well as anthropogenic practices (Yap et al., 2011). Natural sources include: volcanic eruptions, oil seeps, and residential wood burning. Likewise, incomplete combustion of fossil fuel, industrial processing, and petroleum spills can contribute to the release of PAHs into the environment (Gan et al., 2009; Haritash and Kaushik, 2009). The PAHs have become a class of widely distributed environmental contaminants and pose a significant risk to human and ecological health due to their toxicity, persistence, mutagenecity and carcinogenicity. These factors have motivated many scientists to attempt removing them from the environment (Samanta et al., 2002). The US Environmental Protection Agency has identified 16 PAH compounds as the priority pollutants (Atlas and Cerniglia, 1995).

In recent years, various strategies have been proposed for treating wastewater containing PAHs, and these include adsorption, coagulation, flocculation, electrochemical treatment (Swaminathan et al., 2003; Hsueh et al., 2005). However, most of these methods are quite expensive and in many cases they simply transfer the pollutants from one place to another. Hence, there is tremendous interest in using biodegradation technologies for eliminating PAHs due to their environmental safety and comparatively lower cost (Yanto and Tachibana, 2013; Ting et al., 2011). However, biological treatments for PAHs are usually time-consuming and often proved as an incomplete removal process as well (Rehman et al., 2012). In some cases, their metabolites may be more toxic

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http://dx.doi.org/10.1016/j.chemosphere.2015.07.050
0045-6535/

and more difficult to degrade than their parent PAH compounds (Navarro et al., 2011).

To address the limitations of biological remediation and to obtain better PAHs removal efficiency, advanced oxidation processes (AOPs) is an approach as a post-treatment for biological process (Moro et al., 2013). For example, Fenton treatment has received increasing attention as a promising remediation technology for PAH-contaminated aqueous solutions in the last two decades, which has many advantages, such as high efficiency, simplicity, the lack of residues and capacity to treat many different compounds (Hodaifa et al., 2013; Bianco et al., 2011). In the classical Fenton reaction, diluted hydrogen peroxide (H_2O_2) reacts with ferrous ion (Fe^{2+}) in a homogenous solution yielding strong non-specific oxidant hydroxyl radicals ($OH^{\cdot}$) that can react with most organic compounds (Kulik et al., 2006). Fenton-like oxidation using nanoscale zero-valent iron (nZVI) as a catalyst has received much attention in the remediation of pollutants due to its larger specific surface area and higher density of reactive surface sites. This is a significant advantage in its degradation of organic pollutants (Xu and Wang, 2011). Fenton-like oxidation might involve several sequential reactions:

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^- \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \quad (2)$$

The combination of biodegradation and Fenton-like oxidation has a great advantage over either of these two treatments alone in the remediation of PAHs (Gan et al., 2009). Compared with only biodegradation, the degradation time is reduced and a better degradation efficiency of organic pollutants is obtained. More important is that the dosage of nZVI and H_2O_2 decreased and hence reduced the cost, and make it possible for industrial applications (Mandal et al., 2010).

Most studies reported that Fenton-like pre-treatment with subsequent biodegradation enhanced the removal of organic contaminants compared to either one alone (Jagadevan et al., 2012; Mandal et al., 2010; Padoley et al., 2011). However, the extremely low pH requirement (optimum pH 2–3) for the Fenton-like oxidation renders the process incompatible with biological treatment (Yap et al., 2011). In addition, some degraded products from biodegradation of PAHs are toxic (Navarro et al., 2011), while nZVI/H_2O_2 Fenton-like system is often used for the mineralization of the degraded products due to the increasing hydrophilicity of degraded products after the biodegradation of PAHs. In this way, the abiotic processes bridge a gap in the microbial catabolic action to yield complete mineralization of the organic contaminants (Jeon et al., 2013). Hence, a novel remediation strategy consisting of a sequential biodegradation and nanodegradation of naphthalene from aqueous solution was carried out in this study since a coupling the both techniques are superior to individual one for PAHs cleanup.

In our previous study, bacterial strains of *Bacillus fusiformis* (BFN) could be used to biodegrade naphthalene in a cultured medium (Lin et al., 2010a), and Fenton-like treatment has been shown to be effective in mineralizing organic matter. We hypothesized that a biodegradation of naphthalene and mineralization of degraded products are obtained by this coupled treatment. To achieve this objective, the following issues were investigated: (1) studying the growth of BFN and biodegradation of naphthalene and COD removal degree in a cultured medium; (2) investigating the effects of Fenton-like reaction conditions (i.e. pH, nZVI doses, H_2O_2 concentration as well as temperature) on the degradation of organic matter (COD); and (3) discussing the degradation mechanism based on SEM, X-ray diffraction (XRD) and GC–MS.

2. Materials and methods

2.1. Microorganisms and chemicals

The BFN strain was isolated from activated sludge and identified by color and morphology in our previous study (Lin et al., 2010a). The mineral salts medium (MSM) consisted of (g L^{-1}): $K_2HPO_4{\cdot}2H_2O$ 1.0, KH_2PO_4 1.0, NaCl 5.0, $(NH_4)_2SO_4$ 0.3, $MgSO_4{\cdot}7H_2O$ 0.3, $CaCl_2$ 0.020. MSM also contained trace elements as follows: (g L^{-1}): $ZnSO_4$ 5.0, $FeCl_3$ 2.3, $MnSO_4$ 5.0 and $(NH_4)_6Mo_7O_{24}$ 1.0. Flasks containing the medium were sterilized by autoclaving at 121 °C for 20 min.

Nanoscale zero-valent iron (nZVI) was purchased from Hongwu Nano Material Co., Ltd. (Guangdong, China), and with particle size <50 nm, a specific surface area of 40–60 m^2/g and a purity of >99.5%. The naphthalene, n-hexane, ethanol, and remaining chemicals were purchased from Xilong Chemistry Co., Ltd., China. All the chemicals used in this study were analytical reagent grade and used without further purification.

2.2. Biological treatment experiments

The batch naphthalene degradation tests were performed in 100 mL Erlenmeyer flasks sealed with ground glass plugs to minimize possible volatilization. All the bottles were kept in the dark to avoid possible photolysis of naphthalene. Each flask contained 50 mL liquid medium with 0.5% (v/v) inoculums. A series of tests was conducted at naphthalene concentration of 200 mg L^{-1} at neutral pH. The cultures were incubated in a shaking incubator at 150 rpm, 30 °C. The content of the Erlenmeyer flasks have been extracted using 5 mL of n-hexane. The extracts were dried over anhydrous sodium sulfate and evaporated with nitrogen gas to 1 mL prior to GC analysis. The concentration of naphthalene in samples was analyzed using a Varian CP-3800 series GC equipped with a flame ionization detector (FID) and CP-Sil 8 CB column (0.32 mm and 0.25 μm film thickness and length 30 m). The initial column temperature was 50 °C which increased from 50 to 250 °C and then hold for 10 min at 250 °C. Detector and injector temperatures was hold at 300 °C and 250 °C, respectively. High pure grade helium served as the carrier gas with a constant flow rate of 1.0 mL/min. Cell growth was measured based on absorbance at 600 nm with a 722 N spectrophotometer (Bio-Tek Instruments, Shanghai, China). The COD of degraded samples was tested using a water quality detector (LianHua-Tek Instruments, Lanzhou, China) (Kuang et al., 2013). Each experiment was performed in triplicate to ensure data quality.

2.3. Fenton-like oxidation experiment

The batch experiments were carried out in 100 mL Erlenmeyer flasks containing 50 mL naphthalene degradation medium which had be used to cultivate BFN strain for 40 h. The medium's initial pH was adjusted by 1.0 mol L^{-1} H_2SO_4 and 1.0 mol L^{-1} NaOH. In a first approach, Fenton-like process series were operated at constant H_2O_2 concentration: 10 mmol L^{-1}, temperature: 30 °C, nZVI dosage: 0.5 g L^{-1} and various pH value (3.0, 6.0 and 9.0). Following this procedure, the influences of nZVI dosage, H_2O_2 concentration and temperature were examined. Erlenmeyer flasks with the medium and inoculum were then placed on a rotary shaker at 250 r min^{-1}. The variation of COD can be demonstrated as the degradation extent of naphthalene and its metabolites, which was measured at different time intervals (0, 5, 10, 30, 60 min). The pH value was detected using a pH meter (pHS-3, Shanghai, China). All tests were carried out in triplicate.