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Remediation of water contaminated with diesel oil using a coupled process: Biological degradation followed by heterogeneous Fenton-like oxidation

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HIGHLIGHTS

- Diesel oil was removed by biodegradation and Fenton oxidation.
- 78% diesel oil was degraded by *Acinetobacter venetianus* in 96 h.
- Total COD removal increased from 56.8% to 90% by nZVI.
- It is a potential remediation for hard degradable contaminants.

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ABSTRACT

The treatment of a synthetically prepared wastewater containing diesel oil has been investigated using combined treatment schemes based on the biological treatment followed by an advanced oxidation process. 78% of diesel oil was degraded by *Acinetobacter venetianus* in 96 h, while the removal efficiency of chemical oxygen demand (COD) in the aqueous phase was only 56.8%, indicating that degraded metabolites existed in solution. To solve this problem, a Fenton-like system consisting of nanoscale zero-valent iron (nZVI) and hydrogen peroxide was used for further oxidation of the metabolites after biodegradation. Results showed that the total COD removal increased from 56.8% to 89% under the optimal condition. In addition, effects of initial pH (2.0–9.0), ZVI dosage (0–2.0 g L-1), hydrogen peroxide (H_2O_2) dosage concentration (0–15 mmol L-1) and temperature (298–308 K) on the treatment efficiency of the combined process were studied. Scanning electron microscopy (SEM) demonstrated that changes to the surface of nZVI occurred. GC-MS revealed that the degraded metabolites were mineralized practically by nZVI/H_2O_2 system. The results points towards the potential of Fenton-like oxidation as a short post-treatment after a biological process for the treatment of organic pollutants in wastewater.

1. Introduction

With the rapid growth of offshore oil production and transportation, oil spillage and chemical leakage accidents occur worldwide. Such pollutants received particular attention over the last decades due to their mutagenic and carcinogenic properties, and their discharging in significant quantity (Valentine et al., 2010; Gros et al., 2014). Potential environmental risk of oil-contaminated water has been a motivating force in finding sustainable methods for the remediation of these compounds.

To date, broad-spectrum destruction technologies have been applied for treating oil-contaminated waters (Li et al., 2008; Hu et al., 2015; Younker and Walsh, 2015). Among them, biological treatment, in particular, have been shown to be a promising and economic method for the removal of organic pollutants from wastewater based on the natural ability of heterotrophic microorganisms to use hydrocarbons as sole carbon and energy source (Aitken et al., 2004; Smith et al., 2009; Jin et al., 2012; Yang et al., 2016). However, the cycle time of bioremediation for total petroleum hydrocarbons are relatively long and often turned out to be an

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incomplete removal process as well (Sirtori et al., 2009; Ioannou et al., 2015; Xu et al., 2015b). In some cases, the inherent toxicity of the intermediates produced during their degradation compromised the ability of biological method to completely mineralize the pollutants in the wastewater. Therefore, biological treatment techniques, if used alone, have a serious limitation in treating non-biodegradable or toxic chemicals.

To circumvent these problems, investigations on the degradation of organic pollutants are focused on the combination of biological and advanced oxidation processes (AOPs) treatment (Giannakis et al., 2015; Punzi et al., 2015). AOPs are being used as alternative processes for water treatment applications (Xu et al., 2015a). They are based on the generation of strong oxidizing species capable of reacting non-selectively with any organic compound (Giannakis et al., 2015; Moreira et al., 2015b). Of these processes, the Fenton-like process is a mineral-catalyzed system which can be explained by heterogeneous reactions occurring at the surface of iron mineral and hydrogen peroxide in acidic medium. Although the oxidation of diesel oil with Fenton's reagent gains a promising expectation, the homogeneous catalyst such as ferrous salt could be consumed rapidly and low oxidation efficiency was observed. To solve this problem, great efforts have been devoted to developing nanoscale zero-valent iron (nZVI) as a catalyst for heterogeneous Fenton-like oxidation of organic contaminants. It has been found that nZVI can transform various pollutants, including organic chemicals, dyes, heavy metal ions, nitrate, phosphate, and radionuclides due to the advantages of the large surface areas and high reactivity (Zhou et al., 2015). Thus, in the present study, a hybrid method combining the synergistic effects of bacterial treatment, making it amenable for further advanced oxidation processes, was investigated. This integrated system may lead to the total mineralization of organics along with the goal of minimizing the total treatment cost (Moreira et al., 2015a; Ribeiro et al., 2015). Several studies have been performed in which the highly biodegradable component of the wastewater was eliminated biologically and then the recalcitrant contaminants were degraded by AOP application. González et al. (2010) discovered that the sequential biological degradation and advanced oxidation process by using *T. Pubescens* and UV/TiO_2 at a low amount of catalyst allowed up to a 100% chlorophenol removal. Nam et al. (2001) used the combined treatment of the modified Fenton reaction and biodegradation to degrade polycyclic aromatic hydrocarbons (PAHs) in a manufactured gas plant soil and more than 70% of PAHs were mineralized. Pedroza et al. (2007) reported the degradation of generated chlorophenol from the bleaching process during paper production by sequential biological-AOP using *T. versicolor* and UV/TiO_2/Ru_xSe_y, obtaining a 99% chlorophenol removal after 96 h and a 97% reduction in COD. In order to exploit their individual efficacy, reaching thus the desired quality within reasonable economical limits. Efficient treatment of diesel oil contaminated water may require a combination of biological processes and AOP.

In our previous study, *Acinetobacter venetianus* has the ability to degrade diesel oil in a cultured medium (Lin et al., 2015), and Fenton-like oxidation process has been shown to be effective in mineralizing organic pollutants (Li et al., 2015; Yu et al., 2015). In this study the biological degradation, advanced oxidation and the combined biological degradation-advanced oxidation processes for diesel oil was evaluated. For biodegradation assays, whole cells of *Acinetobacter venetianus* were used, while AOP was carried out with the nZVI/H_2O_2 system. For these reasons, the following issues were investigated: (1) studying the biodegradation of diesel oil and COD removal degree in a cultured medium, (2) evaluating the effects of Fenton-like reaction conditions on the further degradation of organic matter, and, (3) discussing the possible mechanism by using various characterizations such as scanning electronic microscopy (SEM), X-ray diffraction (XRD) and gas chromatograph mass spectrometer (GC-MS).

2. Materials and methods

2.1. Microorganisms and chemicals

Diesel oil (density: 0.84 kg L-1) was provided from Fuzhou Petrochemical Co., Ltd. (China). All the other chemicals used in this study were of analytical reagent grade and obtained from Sigma and Aldrich (China). The component of nutrient solution of cell as has been shown in our previous study. Briefly, the composition of mineral salts medium (MSM) solution was as follows: K_2HPO_4 1 g L^{-1}; KH_2PO_4 1 g L^{-1}; NH_4NO_3 1 g L^{-1}; $MgSO_4$ 0.3 g L^{-1}; $CaCl_2$ 0.03 g L^{-1}; $FeSO_4$ 0.005 g L^{-1}; $ZnSO_4$ 0.002 g L^{-1}; $MnSO_4$ 0.0002 g L^{-1}.

2.2. Biodegradation experiments

The biodegradation of diesel oil by *Acinetobacter venetianus* was conducted as follows, the strain was enriched in MSM (30 mL in a 100 mL Erlenmeyer flask) with 50 mg L^{-1} diesel oil being added as the sole carbon source in a dark shaking incubator at 150 rpm for 12 h, 30 °C. We collected the culture suspension from the late log phase culture by centrifuging at 8000 rpm for 10 min. Following this, the cell pellet was washed with sterilized water for three times and adjusted the cell suspension's optical density to 0.7 (OD at 600 nm) using UV–visible spectroscope (Bio-Tek Instruments, Shanghai, China). Initial concentration of diesel oil is 200 mg L^{-1}, 1.5% (v/v) suspension cells was aseptically inoculated into a 150 mL Erlenmeyer flask sealed with ground glass plugs to minimize volatilization. Each flask contained 50 mL liquid medium was placed on a dark shaking incubator at 150 rpm at 30 °C. The residual diesel oil in the flask was extracted using chromatographic grade hexane. The control experiment was conducted by adding MSM into the flask when the initial concentration of diesel oil was 200 mg L^{-1}. The COD concentration of the remaining samples was measured using a water quality detector (LianHua-Tek Instruments, Lanzhou, China). Each experiment was performed in triplicate.

2.3. Fenton-like oxidation experiment

The batch experiments were carried out in a 150 mL Erlenmeyer flasks containing 50 mL diesel oil (initial concentration 200 mg L^{-1}) degradation medium which had been used to cultivate the *Acinetobacter venetianus* for 24 h. After that, the residual aqueous were filtered and centrifuged at 8000 rpm for 10 min to separate strain from liquid, the obtained aqueous were completely transferred to 150 mL Erlenmeyer flasks sealed with ground glass plugs to minimize volatilization. Since the pH value is crucial for the Fenton-like oxidation of organic contaminants, we first studied the pH influence. The initial pH of the medium was adjusted by 0.1 mol/L H_2SO_4 and 0.1 mol/L NaOH. At the very beginning, Fenton-like oxidation treatment was operated at constant H_2O_2 concentration: 10 mmol L^{-1}, temperature: 303 K nZVI dosage: 1.0 g L-1 and various pH value (2.0, 3.0, 6.0, 9.0). Erlenmeyer flasks were then placed on a shaking incubator at 150 rpm. The COD value could be used to reflect the degradation extent of diesel oil and their intermediates, which were detected at different time intervals (0, 10, 20, 30, 40, 50, 60 min).

Following this procedure, the effect of temperature (298, 303, 308 K), initial dosage of nZVI (0.5, 1.0, 1.5, 2.0 g L^{-1}), H_2O_2 concentration (5, 10, 15 mmol L^{-1}) were examined respectively. The effect of temperature on the rates of heterogeneous reactions was used to differentiate the rate-limiting step. The rate constant k at