Bioremediation capability evaluation of benzene and sulfolane contaminated groundwater: Determination of bioremediation parameters

Chu-Fang Yang [a], Shu-Hui Liu [b,c], Yu-Min Su [a], Yu-Rong Chen [a], Chi-Wen Lin [a,d,*], Keng-Li Lin [e]

[a] Department of Safety, Health and Environmental Engineering, National Yunlin University of Science and Technology, 123 University Rd., Sec. 3, Douliu, Yunlin 64002, Taiwan, ROC
[b] Center for General Education, Yu Da University of Science and Technology, 168 Hsueh-fu Rd., Chaochiao Township, Miaoli 36143, Taiwan, ROC
[c] Department of Health Care and Social Work, Yu Da University of Science and Technology, 168 Hsueh-fu Rd., Chaochiao Township, Miaoli 36143, Taiwan, ROC
[d] National Yunlin University of Science and Technology, Taiwan, ROC
[e] National Yunlin University of Science and Technology, Feng Tay Distinguished Professor, Taiwan, ROC

HIGHLIGHTS

- Native sulfolane and benzene degraders were found in a groundwater contamination site.
- Sufficient oxygen supply boosts the removal efficiency of sulfolane and benzene.
- The optimal C:N:P ratio of 100:10:1 was suggested for *in situ* bioremediation application.
- Sulfolane removal was enhanced by adding trace elements and inoculating a bacterial strain.

GRAPHICAL ABSTRACT
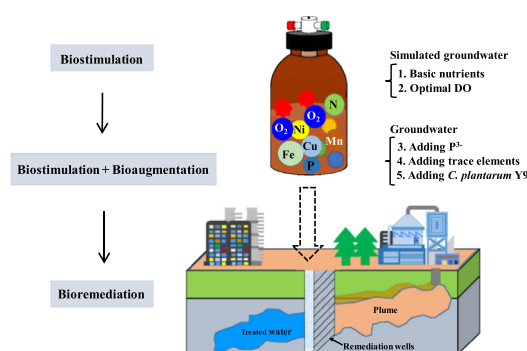
ARTICLE INFO

ABSTRACT

Benzene and sulfolane are commonly used but hazardous chemicals in the petrochemical industry and their leakage and inappropriate disposal certainly causes serious soil and groundwater contamination. In this research, the bioremediation potential of groundwater contaminated with benzene and sulfolane was evaluated, and the operating parameters for bioremediation were established through laboratory batch experiments. Among the various bacterial consortia, the bacterial population of monitoring well c (MWc) contained the highest sulfolane and benzene removal efficiencies. When the dissolved oxygen (DO) level was >1 mg L^{-1}, the bacterial population of MWc showed excellent removal efficiencies toward high and low concentrations of benzene and sulfolane. The C:N:P ratio of 100:10:1 in media facilitated sulfolane and benzene biodegradation, and the degradation time was greatly reduced. Adding additional phosphate into real groundwater could slightly increase benzene removal efficiency. Trace elements only slightly enhanced benzene degradation. On the contrary, additional phosphate and trace elements supplementary did not enhance sulfolane degradation. However, sulfolane removal efficiency could be significantly improved through bioaugmentation of specific sulfolane degrading bacterium and 100% sulfolane removal efficiency was achieved.

© 2018 Elsevier B.V. All rights reserved.

* Corresponding author at: Department of Safety, Health and Environmental Engineering, National Yunlin University of Science and Technology, 123 University Rd. Sec. 3, Douliu, Yunlin 64002, Taiwan, ROC.
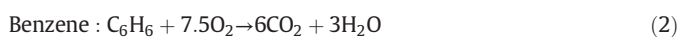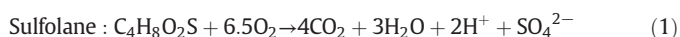E-mail address: Linwen@yuntech.edu.tw (C.-W. Lin).

1. Introduction

Sulfolane (tetrahydrothiophene 1,1-dioxide) is an organic extraction solvent commonly used in the petrochemical industry, and it is widely applied in the extraction of aromatic hydrocarbons, such as benzene, toluene, ethyl-benzene, and xylenes (Chen et al., 2014; Gutiérrez et al., 2018). It is also frequently used to remove acidic gases such as H_2S from gaseous hydrocarbons (Torabi Angaji et al., 2013). Sulfolane has high polarity and solubility. The solubility and log K_{ow} of sulfolane were 1.226×10^6 mg L^{-1} (20 °C) (CCME, 2006) and −0.77 (25 °C) (Yaws, 1994), respectively. Sulfolane may deteriorate water sensory properties and increase oxygen consumption when directly discharged into groundwater. Moreover, it stimulates the central nervous system and inhibits the temperature regulation system in mammals (Bicego et al., 2007; CCME, 2006). The contamination of soil and groundwater with sulfolane is often caused by leakage from plants that process acidic natural gases (Stewart and Minnear, 2010). A long-term groundwater and soil quality-monitoring program focusing on two of the gas processing plants in Alberta indicated sulfolane concentrations varied from 450 to 3400 mg kg^{-1} (soil) and 800 to 1000 mgL^{-1} (groundwater) (Agatonovic and Vaisman, 2015). Sulfolane is not on the list of regulated pollutants for groundwater in Taiwan. However, its concentration is often cooperated into total petroleum hydrocarbons (TPHs), and TPHs standard monitoring concentration of groundwater is 10 mg L^{-1}.

Among petroleum hydrocarbons, benzene is a carcinogenic pollutant and slightly soluble in water (Loomis et al., 2017). The solubility and log K_{ow} of benzene were 1.80 mg L^{-1} (25 °C) and 2.15 (25 °C) (Srivastava and Singh, 2005), respectively. The research indicated that benzene's volatility causes leukemia (Mohammadyan et al., 2016). Thus, benzene is classified as a major pollutant with stringent regulation. The monitoring standard concentration of benzene in groundwater is 0.05 mg L^{-1} in Taiwan. Groundwater often suffers from benzene contamination due to leakage from oil storage tanks and gas stations (Pinedo et al., 2013). The groundwater near Leuna refinery in the North-East of Germany was contaminated by 14.0 ± 2.0 mg L^{-1} benzene (van Afferden et al., 2011). Because benzene and sulfolane are often used in the petrochemical industry, their improper disposal can cause severe groundwater and soil pollution, severely affecting the ecology of neighboring areas.

Activated carbon adsorption is a physical method generally employed for sulfolane and benzene treatment (Wjihi et al., 2017; Ying et al., 1994). Common chemical treatments relied heavily on sulfolane treatment includes chemical oxidation (Izadifard et al., 2018) and photocatalysis (Lhotský et al., 2017; Yu et al., 2016). For benzene chemical treatment, advanced oxidation processes are also highly developed (Tiburtius et al., 2005; Kambhu et al., 2012). However, due to the shortcomings of physico-chemical treatments, such as operational limitations, high energy consumption, high operating costs, and the likelihood of secondary pollution (Padhi and Gokhale, 2014), environmental-friendly and low-cost biological treatment technology is the most preferred treatment and conforms to the current global trend of sustainability. A recent study reported that sulfolane biodegradation was not significant under anaerobic condition, and concluded that oxygen is an important factor limiting natural attenuation of sulfolane plume (Kasanke and Leigh, 2017).

The theoretical amount of oxygen required for the aerobic mineralization of sulfolane and benzene can be calculated using the following chemical equations (Greene et al., 1999):

$$\text{Sulfolane} : C_4H_8O_2S + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + 2H^+ + SO_4^{2-} \quad (1)$$

$$\text{Benzene} : C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \quad (2)$$

Because of high economic benefits and environmental friendliness, bioremediation is the most recommended treatment strategy. Numerous studies on benzene bioremediation have been conducted (Mosmeri et al., 2018; Zouboulis and Moussas, 2011; Chiu et al., 2017; Seeger et al., 2011). However, to our knowledge, studies of sulfolane bioremediation are quite few (Kasanke and Leigh, 2017; Greene and Fedorak, 2001). Moreover, no study is published to simultaneously treat benzene and sulfolane. In this study, the contaminated area was located at the periphery of petrochemical plants and groundwater was contaminated by both benzene and sulfolane. To ensure successful implementation of bioremediation in the target site, the main objectives of this study were to (1) analyze the quality and pollution status of groundwater; (2) confirm the biodegradation potential at the remediation site; (3) determine the optimal dissolved oxygen (DO) level and C:N:P ratio for sulfolane and benzene bioremediation; and (4) assess the applicability of biodegradation schemes for target pollutants in real groundwater in the contaminated area to facilitate integration with subsequent field bioremediation.

2. Material and methods

2.1. The contaminated site and the preliminary remediation system used

In 2013, soil and groundwater around a naphtha-cracking plant in central Taiwan were found to be contaminated by benzene and sulfolane in an area of about 1 ha. The cause of the contamination was speculated to the leakages of an old underground pipeline. Benzene concentration exceeded the second-category groundwater control standard, 0.05 mg L^{-1}, and the concentration of total petroleum hydrocarbons mainly in the form of sulfolane exceeded the hydrocarbon control standard, 10 mg L^{-1}. Fifteen 5–8 m depth monitoring wells were set up at the study site to investigate and remediate the shallow groundwater that flows primarily in a southwest direction. The layout of these wells is shown in Fig. 1. Preliminary remediation actions include dual phase extraction (DPE) and *in situ* chemical oxidation (ISCO) using persulfate and hydrogen peroxide for benzene and sulfolane treatment, respectively. Bioremediation is expecting to conduct in the future for the moderate-to-low concentrations of targeted contaminants.

2.2. Microorganisms and culture media

Mixed cultures used in the experiments were mainly collected from various monitoring wells in the contaminated site. The groundwater sample from each monitoring well was centrifuged at 4°C, 6500 rpm for 10 min, and the pellet was washed several times to obtain indigenous bacterial consortium. Pure sulfolane degrading bacterium, strain *Cupriavidus plantarum* Y9 (accession number: MG725957), used in bioaugmentation experiment was isolated from petrochemical wastewater treatment plant (Liu, 2017).

All bacterial consortia were cultivated in the artificial groundwater media containing benzene and sulfolane as carbon source. The constitutes of the artificial groundwater media (mg L^{-1}) contained K_2HPO_4, 1750; KH_2PO_4, 2145; NH_4Cl, 10; $MgCl_2 \cdot 6H_2O$, 100; $CaCl_2$, 45; $FeCl_3 \cdot 6H_2O$, 1; $CuCl_2 \cdot 2H_2O$, 0.25; $CoCl_2 \cdot 6H_2O$, 0.25; $ZnCl_2$, 1; $MnCl_2 \cdot 4H_2O$, 1; $Na_2MoO_4 \cdot 2H_2O$, 0.1; $NiCl_2 \cdot 6H_2O$, 0.02 (Lin et al., 2015). The trace elements composed of 1 mg L^{-1} $FeCl_3 \cdot 6H_2O$, 0.25 mg L^{-1} $CuCl_2 \cdot 2H_2O$, 0.25 mg L^{-1} $CoCl_2 \cdot 6H_2O$, 1 mg L^{-1} $ZnCl_2$, 1 mg L^{-1} $MnCl_2 \cdot 4H_2O$, 0.1 mg L^{-1} $Na_2MoO_4 \cdot 2H_2O$, 0.02 mg L^{-1} $NiCl_2 \cdot 6H_2O$. The artificial groundwater media were applied in all batch experiments except for nutrient composition and real groundwater experiments. In the nutrient composition experiment, phosphate in the artificial groundwater media was replaced with 0.596 mg L^{-1} Na_2CO_3 and 840 mg L^{-1} $NaHCO_3$. In the real groundwater experiment, K_2HPO_4 and NH_4Cl were added into real groundwater as phosphorus and nitrogen sources, respectively.