Journal of Hazardous Materials 280 (2014) 781–787

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Effect of electrokinetics on biodesulfurization of the model oil by *Rhodococcus erythropolis* PTCC1767 and *Bacillus subtilis* DSMZ 3256

Fatemeh Boshagh, Babak Mokhtarani*, Hamid Reza Mortaheb

Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran

HIGHLIGHTS

- A hybrid technology for desulfurization was studied for the first time.
- *Rhodococcus erythropolis* and *Bacillus subtilis* were studied as microorganisms.
- The yield of biodesulfurization is low and it takes long time to be completed.
- Electrokinetic reduces the process time and accelerates the biodesulfurization.

ARTICLE INFO

Article history:
Received 24 May 2014
Received in revised form 30 August 2014
Accepted 2 September 2014
Available online 16 September 2014

Keywords:
Biodesulfurization
Electrokinetics
Bacillus subtilis
Rhodococcus erythropolis

ABSTRACT

Biodesulfurization of the model oil using *Rhodococcus erythropolis* PTCC1767 (*R. erythropolis*) and *Bacillus subtilis* DSMZ 3256 (*B. subtilis*) strains assisted by applying electrokinetic was investigated as a novel method for desulfurization. The yield of biodesulfurization is low because it takes long time to be completed. Electrokinetic reduces the process time and accelerates degradation of the sulfur compounds. A mixture of normal hexadecane with 10 mM dibenzotiophene (DBT) was employed as the model oil. The biodesulfurization experiments were initially performed. The results represented 34% and 62% DBT conversions after 1 and 6 days by *R. erythropolis* and the biodesulfurization yields were 11% and 36%, respectively. However, the DBT conversions for *B. subtilis* strain after 1 and 6 days were 31% and 55% and the biodesulfurization yields were 9% and 31%, respectively. The electrokinetic biodesulfurization experiments were studied at different current densities and the optimum current density was selected. According to the results, DBT conversion and biodesulfurization yield for *R. erythropolis* after 3 days were 76% and 39%, respectively, at the current density of 7.5 mA/cm^2. At the same conditions, the DBT conversion and biodesulfurization yield for *B. subtilis* were 71% and 37%, respectively. The experimental results indicate that the electrokinetic significantly reduces the biodesulfurization time. The combination of electrokinetic and biodesulfurization has the potential to obtain 'zero sulfur' products.

1. Introduction

Fossil fuels are the most widely used sources of energy in the world, among them, oil has a major contribution of 40% [1,2]. The crude oil is a complex mixture of various compounds with sulfur content of 0.03–7.89% (w/w) [3–6]. Vast release of sulfur oxide (SO_2) due to combustion of fossil fuels can cause adverse effects on health, environment, and economy [4]. Nowadays, the strongest incentive for the reduction of sulfur in the fuels is the rigorous environmental regulation [1–7]. The simplest way to decrease the amount of SO_2 is to limit the amount of sulfur in the fossil fuels [3]. The pre- and post-combustion treatment methods can be used to reduce the amount of SO_2 emissions [4]. The pre-combustion method includes physical, chemical, and biological processes (biodesulfurization) [8]. Hydrodesulfurization (HDS) is the most commonly established physico-chemical technology to reduce the sulfur content of the crude oil. This process is very costly due to utilization of hydrogen gas and metal catalysts (Co/Mo, Ni/Mo), and high operating temperature (200–425 °C) and pressure (150–250 psi H_2). In addition, the method is not effective for removing heterocyclic organosulfur compounds [4]. Biodesulfurization (BDS) is an environmental friendly method that can specifically remove sulfur from refractory hydrocarbons under mild conditions without lowering the calorific value of the fuel. BDS has the potential to satisfy the new stringent standards. However, the application of BDS is limited because of its slow biodegradation rate [1,4].

---

* Corresponding author. Tel.: +98 21 44580751; fax: +98 21 44580781.
E-mail address: mokhtaranib@ccerci.ac.ir (B. Mokhtarani).

http://dx.doi.org/10.1016/j.jhazmat.2014.09.006
0304-3894/

Dibenzothiophene (DBT) is the most employed substance as a model feed containing sulfur compounds that are difficult to be removed using HDS [9,10]. The specific sulfur pathway, which selectively cleavages sulfur compounds without breaking the carbon skeleton, is called the '4S' pathway. DBT is converted to 2-hydroxybiphenyl (2-HBP) and sulfite through the 4S pathway [1–5,11].

Electrokinetics (EK) is defined as the physicochemical transport of charge, action of charged particles, and effects of applied electrical potentials on fluid transport in a porous media. Electrokinetics is induced through one of the several transport mechanisms (electromigration, electroosmosis and electrophoresis) and electrochemical reactions (electrolysis and electrodeposition) using a low direct current as the "cleaning agent" [12,13]. Electrokinetic remediation is a green remediation technology developed in recent decades for the purpose of separating and extracting heavy metals, radionuclides, and organic contaminants from saturated or unsaturated soils, sludges, sediments, and groundwater [14–17]. This emerging technology is substantially based on a low-level direct current of the order of mA/cm^2, which crosses the area comprised between the electrodes to remove contaminants [18–20]. The EK is affected by many factors such as pH, temperature, soil type, moisture content, voltage and current, nature of electrodes, contaminant type, and processing time [13,17,18]. Electrokinetic can be coupled to other technologies in order to maximize contaminant removal. The combination of EK and biological techniques can compensate the deficiencies of each technique and thus increases remediation efficiency and decreases remediation time. Nutrients, contaminant, and bacteria can be conveyed efficiently by EK technique that not only increases the biomass of bacteria and enhances their activity and growth [14,21], but also results in an overall homogenization for the reaction partners [16,22]. Several efforts have been made to combine EK and bioremediation processes for effective biodegradation [15,23–25]. However, there is no report on the impact of EK on BDS.

Electroosmosis causes the movement of pore water from the anode toward the cathode while electromigration and electrophoresis transfer ions and charged particles including microorganisms toward the electrode of the opposite charge [24–26]. These mechanisms can transport the contaminants, degrading bacteria, bacterial nutrients, and even pore fluids and thus have the potential to accelerate the mass transfer and the interactions among contaminants, bacteria, and bacterial nutrients during process [25]. In the present research, the combination of electrokinetics and BDS is studied for the first time. It comprises the induction of an electrical field on the acting media of microorganisms for removing the sulfur content. BDS (similar to other microbial processes) is limited by the slow biodegradation, takes long time to be completed, and has low desulfurization yields [1,4]. As BDS is a reaction in the two-phase (oil-water) system, one of the major obstacles is the limited access of microorganism (aqueous phase) to the hydrophobic organic contaminant (organic phase) [9]. The problem of bioavailability can be overcome by using electrokinetics and enabling faster contaminant transfer to the bacteria or enhancing the mobility of bacteria [16].

The effects of electrokinetic on BDS of model oil are studied using *Rhodococcus erythropolis* PTCC1767 and *Bacillus subtilis* DSMZ 3256. Desulfurization of the model oil is initially evaluated by the BDS experiments. The combined electrokinetic-BDS experiments are then performed. The model aquifer system under constant-temperature and pH is employed. The effects of electric current density on the DBT conversion and desulfurization yield are investigated.

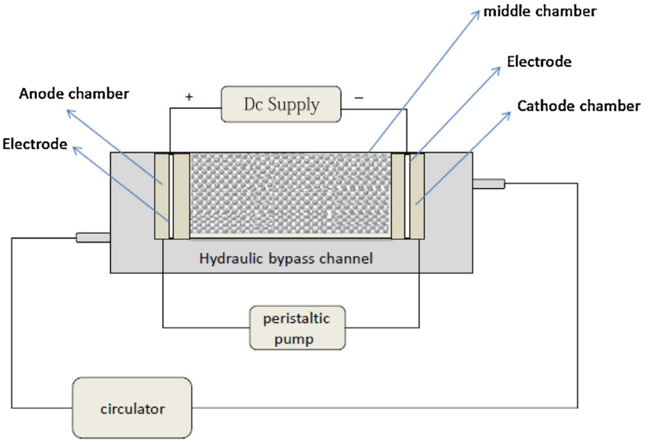

Fig. 1. Schematic diagram of electrokinetic setup.

2. Materials and methods

2.1. Chemicals and microorganisms

All chemicals were obtained from Merck (Germany) unless otherwise stated. *R. erythropolis* PTCC 1767 and *B. subtilis* DSMZ 3256 were purchased from Persian Type Culture Collection and German Type Culture Collection, respectively. The strains were kept in lyophilized state at −70 °C in glycerol stocks.

2.2. Medium and growth conditions

R. erythropolis and *B. subtilis* were separately cultured in basal salt medium (BSM). The preculture was performed in Luria-Bertani (LB) medium for 24 h at 200 rpm and incubated in shaker incubator (Kuhner, Switzerland) at 30 °C. After primary cultivation, 4% inoculation was performed into the BSM medium with the composition of (g/L): NaH_2PO_4, 4; K_2HPO_4, 4; $MgCl{\cdot}6H_2O$, 0.0245; $CaCl_2{\cdot}2H_2O$, 0.0006; $FeCl_3{\cdot}6H_2O$, 0.001; glucose, 20; $(NH_4)_2NO_3$, 2 and glycerol 2% (v/v). DBT (as a sole sulfur source) was also dissolved in ethanol (100 mM) and added to the sterilized BSM with a final concentration of 2 mM in the medium. The BSM medium was cultivated at 200 rpm, 30 °C and pH 7.

2.3. Electrokinetic apparatus and setup

The electrokinetic setup is shown in Fig. 1. It consists a horizontal rectangular plexiglass reactor (30 cm × 11 cm × 7 cm) divided into four compartments: two electrode chambers (3 cm × 5 cm × 5 cm) at both ends, a middle chamber (18 cm × 5 cm × 5 cm), and a bypass channel (30 cm × 11 cm × 7 cm) beneath the middle compartment having hydraulic contact with the both electrode compartments. 4-mm diameter glass beads (Merck) were placed in the middle chamber as the packing material. Stainless steel electrodes (0.2 cm × 4 cm × 4 cm) were inserted in both sides with 2 cm distance from the walls. Inlet and outlet valves were mounted at each front end of the apparatus. The anode and cathode were connected to a DC power supply (max. 30 V, 0.01–1 A). 0.1 mM potassium phosphate buffer (pH 7.4) was used as the electrolyte in both the cathode and anode compartments. Temperature and pH were controlled during the experiments. A peristaltic pump (Heidolph, PD5006, Germany) was used to circulate the electrolyte solution from cathode to anode at a rate of 30 ml/min to control ionic concentrations and sudden pH change in bioreactor. Temperature was controlled at 30 °C using a circulator (Julabo HL, FP50, Germany), which circulates the water in bypass channel of the reactor. pH and temperature were determined at the final sampling time. At the