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Short communication

Deep desulfurization of diesel by integrating adsorption and microbial method

Wangliang Li*, Huang Tang, Qingfen Liu, Jianmin Xing*, Qiang Li, Dan Wang, Maohua Yang, Xin Li, Huizhou Liu

National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, P.O. Box 353, Beijing 100080, China

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ABSTRACT

Aiming for the deep desulfurization of diesel, a novel adsorption–bioregeneration system was constructed by combining adsorption and biodesulfurization processes. The sequence of adsorption capacity of DBT (dibenzothiophene) is AC (activated carbon) > NiY > AgY > alumina > 13X. The sequence of selectivity of DBT toward naphthalene is NiY > AgY > alumina ≈ 13X > AC. For hydrotreated diesel, MAS (mesoporous aluminosilicates) showed high adsorption capacity, while MCM-41 and NaY showed low adsorption capacity. The bioregeneration process of these adsorbents was also carried out with *P. delafieldii* R-8 cells. Adding *P. delafieldii* R-8 cells can improve DBT desorption from adsorbents. The desorption of DBT from adsorbents by bioregeneration follows the sequence: 13X > alumina > AgY > NiY > AC. Ag-MAS can be completely regenerated in *in situ* adsorption–bioregeneration system.

1. Introduction

To meet strigent emission standard stipulated by regulatory organics, ultra-deep removal of sulfur from transportation fuels has become very imperative for the petroleum refining industry. Although hydrodesulfurization (HDS) is a conventional method to remove sulfur compounds for industrial purpose, it is difficult to remove some hetercyclic sulfur compounds such as dibenzothiophene (DBT) and substituted DBTs in petroleum [1]. In order to achieve the "no sulfur" specification, some new technologies such as adsorption desulfurization [2–4], biodesulfurization [5], extraction desulfurization with ionic liquids [6–8] and complex formation desulfurization [9,10] were proposed.

Modified Y-type zeolite was popularly used as adsorbents to remove sulfur from fuels via π-complexation. Yang and co-workers reported that Cu(I) and Ag-exchanged Y-typed zeolites were effective to remove sulfur compounds from gasoline [11–13]. Song et al. reported the selective adsorption process for removing sulfur (SARS) at ambient temperature to achieve ultra-clean diesel and gasoline with NiY [4,25–27]. Mekinley et al. reported selective removal of DBT and 4,6-DMDBT from simulated feedstock with Ag^+/SBA-15 and Ag^+/SiO_2 as adsorbents [18]. Adsorption desulfurization has some problems to be solved. When the selectivity is low, the adsorbents are easy to be regenerated. But this can lead to the heat loss because of the comparative adsorption. As the selectivity increases, the spent adsorbents become more and more difficult to be regenerated [14–17]. Adsorbents should be well designed to achieve suitable selectivity. Solvent extraction and calcination in the air are two methods to regenerate the desulfurization adsorbents. There are some disadvantages in these two methods. For solvent extraction method, it is difficult to separate sulfur compounds from the organic solvents and reuse these solvents. And for calcinations method, sulfur compounds and aromatics are burned out which can lose heat value of fuels.

Another approach to produce ultra-low fuels is biodesulfurization (BDS) which can selectively remove sulfur from DBTs. BDS has the potential benefits of lower operation cost and production of valuable byproducts. Sulfur compounds can be converted into hydroxylbiphenyl and its derivatives [5,19,20]. BDS can be considered either an alternative or a complementary method to the conventional oil refining technology. Some of the isolated microorganism capable of sulfur removal are not effective in commercial uses. Therefore, there is still a need to increase the rate of sulfur removal that may efficiently biodesulfurize the diesel [5,20].

We proposed a method to produce ultra-low sulfur diesel by adsorption and biodesulfurization, that is, to regenerate adsorbents with microbial cells [21]. Bioregeneration is the renewing of activated carbon by microbial activities. Bioregeneration can be achieved either by mixing bacteria with saturated activated carbon in offline systems and was widely used in wastewater treatment and organic removal [22]. AC (activated carbon), alumina and zeolite are commonly used adsorbents in industrial processes [23]. The adsorption and bioregeneration properties of the adsorbents

* Corresponding authors. Tel.: +86 10 62550913; fax: +86 10 62550913.
E-mail addresses: wlli@home.ipe.ac.cn (W. Li), jmxing@home.ipe.ac.cn (J. Xing).

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were studied with selected *P. delafieldii* R-8 strains. Micropore of Y zeolite can be blocked by polyaromiatics. Desulfurization from hydrotreated diesel of mesoporous materials MAS and MCM-41 was studied. Desulfurization properties of MAS, NaY and MCM-41 were conducted with 207 $\mu g\,g^{-1}$ hydrotreated diesel. Adsorption and bioregeneration properties of Ag-MAS were reported with hydrotreated diesel in *in situ* system.

2. Materials and methods

2.1. Chemicals

13X, NaY zeolite and activated alumina were kindly provided by Catalyst Plant of Qilu Petrochemical Company CNPC. Methanol was HPLC grade. Other chemicals were of analytical reagent grade and commercially available.

2.2. Adsorbents preparation

AgY was prepared by ion-exchanging method according to the literature reported by Hernández-Maldonado and Yang [24].

NiY was prepared by ion-exchanging method according to the literature reported by Song and co-workers [25–27]. Before using, NiY were pre-reduced in a flowing reactor under a reducing gas (5%H_2 and 95%N_2) with a flow rate 80 mL min^{-1} at 640 °C for 6 h, and then passivated using sulfur-free *n*-octane and stored in the same solvent in an airtight sample bottle.

MCM-41 with Si/Al ratio of 50 was synthesized following the procedure given in Ref. [28] using CTAB (cetyltrimethylammonium bromide, purity > 99%) as structure directing agent, sodium silicate solution as silica source and pseudobohemite (Catapal B) as aluminum source.

MAS was synthesized by two-step method [29]. Nanocluster zeolite Y seeds were prepared by reacting NaOH (0.088 mol) and $NaAlO_2$ (0.10 mol) in H_2O (8.5 mol) with silicate anions (0.9 mol) in the form of sodium silicate solution. The clear solution was aged overnight. Then the seed solution was added to the CTAB (0.27 mol) solution. The pH value was lowered to 10 with sulfuric acid. The mixture was placed at 100 °C for 24 h. The MAS was calcinated in a N_2 atmosphere at 550 °C for 1 h followed by 6 h calcinations in the air at the same temperature.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded by a Shimadzu XD-3A diffractometer equipped with Cu Ka radiation (k = 0.154 nm) and Ni filter and operated at 40 kV and 40 mA.

The Brunauer–Emmett–Teller (BET) surface areas and N_2 sorption isotherms were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2010 analyzer.

Desorption properties of the adsorbents were studied with thermogravimetric–differential thermal analysis (TG–DTA) which was carried out in SP-4320 thermal balance (Shanghai Precision Scientific Instruments Co. Ltd.). The sample was heated to 150 °C in flow of inert gas (N_2) for 2 h to remove water and solvent *n*-octane. About 20 mg of adsorbents was loaded and the N_2 flow used was 50 mL min^{-1}. The heating rate was 10 °C min^{-1} and the final temperature was 700 °C.

2.4. Bacterial strain and cultivation

P. delafieldii R-8 (CGMCC 0570) was isolated from the sewage pool of Shengli Oil Field of China. *P. delafieldii* R-8 can be cultured in a standard medium (BSM) reported in the literature [5].

Table 1
Physical properties of hydrotreated diesel.

	Density ($g\,cm^{-1}$)	n_d^{20}	Sulfur ($\mu g\,g^{-1}$)	Nitrogen ($\mu g\,g^{-1}$)	Aromatics content (%)
WL-1	0.826	1.459	91	2.8	16
WL-2	0.825	1.458	79	2.1	16
WL-2	0.825	1.458	63	1.2	18

n_d^{20}, refractive index.

P. delsfieldii R-8 was cultured in BSM. The formulations of the mentioned media are as follows: KH_2PO_4 2.44 g L^{-1}, $Na_2HPO_4{\cdot}12H_2O$ 12.03 g L^{-1}, $MgCl_2{\cdot}6H_2O$ 0.4 g L^{-1}, NH_4Cl 2.0 g L^{-1}, $CaCl_2$ 0.75 mg L^{-1}, $FeCl_3{\cdot}6H_2O$ 1 mg L^{-1}, $MnCl_2{\cdot}4H_2O$ 4 mg L^{-1}, glycerol 10 g L^{-1}. 1 mmol L^{-1} DBT was added as the sulfur source. Cell cultivation was carried out at 30 °C on a rotary shaker operated at 170 rpm.

Cells were harvested in the late logarithmic phase by centrifugation at 5000 rpm for 5 min. The cell pellets were washed twice with saline, lyophilized and kept below −20 °C.

2.5. Adsorption methods

The adsorption capacity and selectivity towards DBT of the adsorbents were tested under ambient conditions with 8.0 mmol L^{-1} DBT and 8.0 mmol L^{-1} naphthalene in *n*-octane. The adsorption was operated at 30 °C with equilibrium method. The ratio of oil to adsorbent was chosen as 100 mL g^{-1}.

Adsorption properties of Ag-MAS, Ag-MCM-41 and Ag-Y were tested with hydrotreated diesel at 30 °C. Ratio of adsorbents to oil is 20 mL g^{-1}. Table 1 shows the physical properties of hydrotreated diesel.

2.6. Regeneration of adsorbent

The regeneration system contained *n*-octane, aqueous phase, lyophilized cells and spent adsorbents. All reactions were carried out in 100 mL flasks at 30 °C on a rotary shaker operated at 200 rpm.

Adsorption–bioregeneration properties were tested in *in situ* adsorption–bioregeneration system. Fig. 1 shows the scheme of the system. The system can be divided into two parts: adsorption and bioregeneration. After the saturation of adsorbents, the adsorption system is shut up and adsorption reactor was connected with bioreactor. Then the desorbed sulfur compounds were converted by *P.*

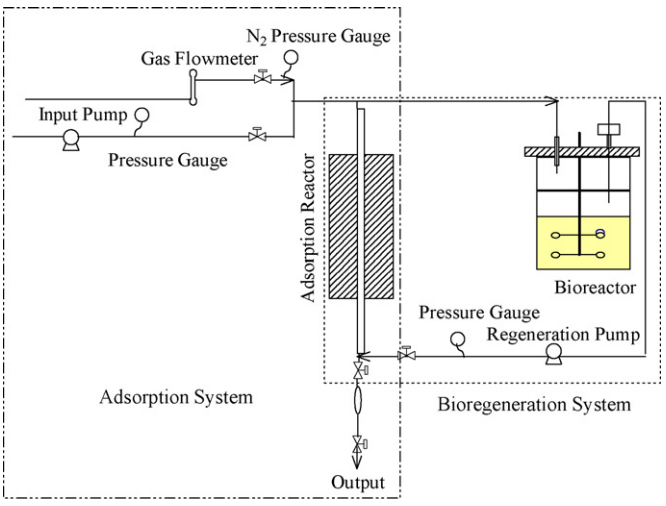

Fig. 1. Schematic diagram of *in situ* adsorption–bioregeneration system.