1. Introduction

To meet stringent 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-type 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-DMD BT from simulated feedstock with Ag+/SBA-15 and Ag+/SiO2 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 hydroxyl biphenyl 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
were studied with selected \textit{P. delafeldii} R-8 strains. Micropore of Y zeolite can be blocked by polyaromatics. 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 \textit{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\%\( \text{H}_2 \) and 95\%\( \text{N}_2 \)) with a flow rate 80 mL min\( ^{-1} \) at 550\( ^\circ \text{C} \). The regeneration was carried out in SP-4320 thermal balance (Shanghai Precision Scientific Instruments Co. Ltd.).

MAS was synthesized by two-step method [29]. Nanocluster zeolite Y seeds were prepared by reacting NaOH (0.088 mol) and NaAIO\(_2\) (0.10 mol) in \( \text{H}_2\text{O} \) (8.5 mol) with silicate anions (0.9 mol) in the form of sodium silicate solution. The pH value was lowered to 10 with sulfuric acid. The mixture was heated to 150\( ^\circ \text{C} \). Powder X-ray diffraction (XRD) patterns were recorded by a Shimadzu XD-3A diffractometer equipped with Cu Ka radiation (\( k=0.154 \text{nm} \)) 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 \( ^\circ \text{C} \) 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 \( ^\circ \text{C} \) min\( ^{-1} \) and the final temperature was 700\( ^\circ \text{C} \).

2.3. Characterization

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

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 carried out at 30 \( ^\circ \text{C} \) with equilibrium method. The ratio of oil to adsorbent was chosen as 100 mL g\( ^{-1} \).

Adsorption–bioregeneration properties were tested in \textit{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 \( P. \) delafeldii R-8 on a rotary shaker operated at 170 rpm.

2.4. Bacterial strain and cultivation

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

Table 1

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Density} & \textbf{\( \rho_2^\circ \)} & \textbf{Sulfur} & \textbf{Nitrogen} & \textbf{Aromatics content} \\
\textbf{(g cm\(^{-3}\))} & \textbf{(\( \mu \text{g} \text{ g}^{-1} \))} & \textbf{(\( \mu \text{g} \text{ g}^{-1} \))} & \textbf{(\( \mu \text{g} \text{ g}^{-1} \))} & \textbf{(\%)} \\
\hline
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 \\
\hline
\end{tabular}
\caption{Physical properties of hydrotreated diesel.}
\end{table}

\( \rho_2^\circ \), refractive index.

\( P. \) delafeldii R-8 was cultured in BSM. The formulations of the mentioned media are as follows: \( \text{KH}_2\text{PO}_4 \) 2.44 g L\(^{-1} \), \( \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \) 12.03 g L\(^{-1} \), \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) 0.4 g L\(^{-1} \), \( \text{NH}_4\text{Cl} \) 2.0 g L\(^{-1} \), \( \text{CaCl}_2 \) 0.75 mg L\(^{-1} \), \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) 1 mg L\(^{-1} \), \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \) 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 \( ^\circ \text{C} \) 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 \(-20^\circ \text{C} \).

2.5. Adsorption methods

The regeneration system contained \( n\)-octane, aqueous phase, lyophilized cells and spent adsorbents. All reactions were carried out in 100 mL flasks at 30 \( ^\circ \text{C} \) on a rotary shaker operated at 200 rpm.

Adsorption–bioregeneration properties were tested in \textit{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 \( P. \) delafeldii R-8 on a rotary shaker operated at 170 rpm.

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 \( ^\circ \text{C} \) on a rotary shaker operated at 200 rpm.

The regeneration system is 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 \( P. \) delafeldii R-8 on a rotary shaker operated at 170 rpm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Schematic diagram of \textit{in situ} adsorption–bioregeneration system.}
\end{figure}
delafeldii R-8 cells. Finally, the desorbed adsorbents was treated with air at 550 °C to remove water from adsorption system.

2.7. Analytical methods

High-performance liquid chromatography (HPLC) was used for the quantitative assay of DBT and 2-HBP in the n-octane phase. HPLC was performed on a Agilent 1100 (HP1100, Agilent, USA) liquid chromatography equipped with an autosampler, a reversed-phase Zorbax SB-C18 column (4.6 mm × 150 mm; 3.6 μm) and a diode array detector. The mobile phase was 90% of methanol in water (v/v, %) with a flow rate of 1.0 mL min⁻¹. For the quantification of DBT and 2-HBP, the external standard method was used at 280 nm. The total sulfur content (by weight) was determined in triplicate for each sample by combustion of samples and measurement of the released sulfur dioxide using a microcoulomb analyzer (RPA-200, JiangHuan Electroanalysis, China).

3. Results and discussions

3.1. Characterization of adsorbents

From XRD pattern of MCM-41 and MAS, it can be observed in Fig. 2 that three resolved peaks at 2θ from 0.5 to 5 that can be indexed to 100, 110 and 200. It can be deduced that MCM-41 and MAS exhibit hexagonal arrays with uniform pore size.

The texture properties were characterized by nitrogen adsorption–desorption analysis. The results are summarized in Table 2. It can be observed that MCM-41 and MAS possess mesoporous structure. Both of surface area and pore diameter are larger than NaY zeolite. Under room temperature, ion-exchanging process has slight effects on the textural properties of the adsorbents. Therefore, compared with modified Y zeolite, mass transfer can be improved with modified mesoporous materials as adsorbents.

3.2. Adsorption process

Adsorption capacities such as adsorption capacity and selectivity of adsorbents 13X, alumina, Ag-Y and Ni-Y were observed with 8.0 mmol L⁻¹ DBT and 8.0 mmol L⁻¹ naphthalene as model compounds. Ratio of oil to adsorbents was chosen as 80 mL g⁻¹. As can be seen in Table 3, adsorption capacity of these adsorbents follows the sequence: AC > NiY > AgY > alumina > 13X. The selectivity of DBT over naphthalene follows the sequence: NiY > AgY > 13X ≈ alumina > AC. Adsorption properties of NaY, MCM-41 and MAS towards hydrotreated diesel were carried out at 30 °C. Ratio of oil to adsorbents was 20 mL g⁻¹. As shown in Table 4, the adsorption desulfurization properties of Ag-MAS are much better than Ag-MCM-41. Adsorption desulfurization properties of Ag-MAS and Ag-MCM-41 are much better than those of Ag-Y. The main reason is that large molecular compounds in the diesel can block the pores of Ag-Y, thus, desulfurization potential decreases sharply.

3.3. TG–DTA characterization

Desorption of DBT from different adsorbents were characterized by TG–DTA. Fig. 3 shows TG desorption profiles of DBT on different adsorbents. It can be seen that desorption capacity of DBT follows the sequence: AC > NiY > AgY > Al₂O₃ > 13X. The interaction forces of DBT and adsorbents can be observed in Fig. 3. AC profile continues to decrease even when the temperature is higher than 400 °C, but for that of 13X almost remains stable after 200 °C. It can be deduced that the interaction of DBT with AC is much stronger than

### Table 2

| Textural properties of adsorbents MAS, MCM-41 and NaY. |
|-----------------|---------------|---------------|
|                  | MCM-41        | MAS           | NaY           |
| Pore diameter (nm) | 3.51          | 3.27          | 0.79          |
| Pore volume (cm³ g⁻¹) | 0.79          | 0.82          | 0.34          |
| Surface area (m² g⁻¹) | 940           | 906           | 647           |

### Table 3

| Results of adsorption of DBT and naphthalene on different adsorbents. |
|-----------------|---------------|---------------|---------------|
| Adsorbents      | Activated carbon | reduced NiY | AgY | 13X | Alumina |
| DBT (mmol g⁻¹) | 0.324          | 0.286        | 0.237 | 0.033 | 0.042  |
| Naph (mmol g⁻¹) | 0.272          | 0.149        | 0.161 | 0.026 | 0.034  |
| Selectivity     | 1.191          | 1.915        | 1.472 | 1.269 | 1.235  |

A_{DBT}, amount of DBT adsorbed per gram adsorbents; A_{Naph}, amount of naphthalene adsorbed per gram adsorbents.

### Table 4

| Sulfur content of products (μg g⁻¹). |
|-------------------------------|----------------|---------------|
|                               | WL-1            | WL-2          | WL-3          |
| Ag-Y                          | 38              | 37            | 23            |
| Ag-MAS                        | 24              | 16            | 11            |
| Ag-MCM-41                     | 32              | 24            | 19            |

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According to the observations, the interaction of DBT with different adsorbents follows the sequence: AC > NiY > AgY > alumina > 13X.

3.4. Bioregeneration process

The adsorbents can be regenerated by bioregeneration method. The effect of adding *P. delafieldii* R-8 cells on the DBT desorption has been studied. The ratio of water to adsorbent is 60 mL g\(^{-1}\) and the phase ratio of water to oil is 1/6 (v/v). From Fig. 4, it can be seen that the desorption ratio is higher when adding desulfurization cells. During the regeneration process, most of DBT molecules adsorbed can be desorbed from the surface of adsorbent by contacting with oil phase. A part of DBT molecules can enter the aqueous phase directly. DBT molecules can be converted into 2-HBP and sulfate by microbial cells at the oil/water interface and in the aqueous phase. The decrease of DBT concentration in oil phase can promote DBT desorbing from the surface of adsorbent. Thus adding *P. delafieldii* R-8 cells can improve DBT desorption.

As we reported previously, during the process of bioregeneration, desorption of DBT can be significantly improved by adding oil phase [20]. Adsorbents were bio-regenerated when the volume ratio of oil-to-water was 1/5, the cell concentration was 50 g L\(^{-1}\), and the ratio of water-to-adsorbent was 60 g mL\(^{-1}\). Fig. 5 shows the desorption of DBT from different adsorbents with microbial method. The sequence of DBT desorption ratio is 13X > alumina > AgY > NiY > AC. This means that the stronger interaction of DBT with adsorbent, the more difficult to be desorbed. For AC, the interaction of DBT with adsorbents is so strong that only little DBT can be desorbed.

The bioregeneration and recycling properties of Ag-MAS were also achieved with 79/74 H9262 gg\(^{-1}\) hydrotreated diesel. *n*-Octane was chosen as regeneration solvent. Ratio of *n*-octane to adsorbent Ag-MAS is 5 mL g\(^{-1}\). Fig. 6 shows adsorption properties of fresh and regenerated adsorbents Ag-MAS. Regenerated adsorbents has similar adsorption properties with fresh ones. Spent Ag-MAS can be regenerated in the integrated system.

4. Conclusion

Adsorbent NiY has the highest selectivity towards DBT and AC has the largest adsorption capacity. For hydrotreated diesel, MAS has better desulfurization ability than NaY and MCM-41. DBT desorption from adsorbents can be improved by adding *P. delafieldii* R-8 cells. The desorption of DBT from adsorbents follows the sequence: 13X > alumina > AgY > NiY > activated carbon. Spent adsorbent Ag-MAS can be regenerated on the integrated system. Adsorption property of regenerated Ag-MAS is similar to fresh Ag-MAS.

The integrated system is able to desulfurize DBT more efficiently than other methods. The role of with respect to various factors, such as effect of the amount of aromatics, separation of adsorbents and cells, will be detailly investigated.
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References


