



A pilot trial for fast deep desulfurization on MOF-199 by simultaneous adsorption-separation via hydrocyclones



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ABSTRACT

Deep removal of organic sulfur from fuel has become an important issue worldwide in the field of energy and environment. In this work, a novel approach for efficient adsorption-desulfurization in which both the adsorption and separation processes were performed simultaneously was demonstrated in a two-stage hydrocyclones pilot trial. We applied mass-produced MOF-199 as the adsorbent and dibenzothiophene (DBT) dissolved in dodecane as the model fuel. The adsorption dynamics and the significant influences of the dosage of adsorbent, the inlet flow rate and the split ratio on the removal efficiency were investigated to match the simultaneous adsorption-separation processes. After optimizing the operating conditions, the ultimate DBT concentration in the outlet of the two-stage hydrocyclones was 8.79 ppmw, which was less than the regulatory target of 10 ppmw; the separation efficiency of MOF-199 particles was as high as 99.75% within 30 s at an initial DBT concentration of 50 ppmw and a dosage of MOF-199 of 5 wt.%. More importantly, MOF-199 can be successfully regenerated using H₂O₂ oxidation at the laboratory scale. The exceptionally high removal efficiency, fast separation speed, low cost and simple equipment make this simultaneous adsorption-separation hydrocyclone process a promising deep-desulfurization method.

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1. Introduction

Deep desulfurization is of great concern worldwide because sulfur compounds are a major source of acid rain and air pollution [1]. By 2017, Environmental Protection Agency (EPA) regulations require that the total sulfur content in federal gasoline not exceed 10 ppmw, whereas they limit that in ultra-low sulfur diesel (ULSD) to 15 ppmw [2]. Additionally, European Union environmental regulations have limited the level of total sulfur in both gasoline and diesel to less than 10 ppmw [3,4]. A common goal of deep desulfurization methods is to limit the total sulfur levels in fuels to 10 ppmw worldwide.

The organic sulfur compounds in fuels consist of thiols, sulfides and aromatic sulfur compounds, such as thiophene (TS), benzothiophene (BT), and their alkylated derivatives. Aromatic sulfur compounds comprise ~70% of the total organic sulfur in fuel [5–7]. Currently, the most common industrial technology to remove sulfur compounds is hydro desulfurization (HDS) [8,9]. However, it is

less effective for removing refractory sulfur compounds, such as dibenzothiophene (DBT) and its derivatives [10,11]. In addition, operating conditions with high temperatures and high pressures (hydrogen pressure greater than 2 MPa and temperature above 300–400 °C) are usually costly, especially for deep desulfurization [12,13]. Moreover, HDS also leads to the loss of fuel quality to some degree because of the reduction of the octane number caused by side reactions [14,15]. To meet the demand of deep desulfurization, many desulfurization technologies have been explored, such as biodesulfurization (BDS) [16,17], extraction (EDS) [18–21], oxidative desulfurization (ODS) [22,23], and adsorptive desulfurization (ADS) [24–26]. Among them, ADS has been the most promising technique owing to its ability to process sulfur-free liquid fuels under ambient conditions; this method offers high efficiency, low energy consumption and easy operation. Various types of adsorbents, such as carbon, alumina, zeolites and other novel porous materials [27–30], have been used for ADS. Recently, MOF-199 [31,32], a widely studied metal-organic framework (MOF) material, has exhibited good adsorption capacity in the desulfurization process because of its large specific surface area and its strong affinity to organic sulfur caused by acid-base interactions,

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Nomenclature

Re	inlet Reynolds number of the hydrocyclone, $Re = \rho Dv/\mu$	p_i, p_o	the pressure in the inlet and overflow of the hydrocyclone (MPa)
Eu	inlet Euler number of the hydrocyclone, $Eu = \Delta P/(\frac{1}{2}\rho v^2)$	Δp	the pressure drop between the inlet and overflow of the hydrocyclone (Pa)
R_f	flow split of the hydrocyclone, $F = Q_{ii}/Q_i \times 100\%$ (%)	Greek letters	
v	velocity of the hydrocyclone (m s^{-1}), $v = 4Q_i/\pi D^2$	μ	the viscosity of the liquid medium (mPa s)
D	diameters of swirl chamber (mm)	ρ	the density of the liquid medium (kg m^{-3})
Q_{ii}, Q_i	individually the volume flow of the underflow and feed ($\text{m}^3 \text{s}^{-1}$)		

π -complexation, direct metal-sulfur interaction and van der Waals forces [33–36]. However, all the above reported works were still in the laboratory stage because separation of dispersed MOF-199 powders from suspensions remains very difficult, which seriously limits the commercial applications of ADS.

Fixed beds and fluid beds are the most common technologies for separating solid particles from suspensions to obtain a final clean fuel [37,38]. However, with a size in the range of 5–100 μm , the close packing of small MOF-199 particles in fixed beds will increase the resistance significantly, and also reduce the contact between the solid phase and liquid phase and hence limit the adsorption efficiency. Whereas, the fluid bed requires enormous energy input and easily causes liquid flooding and particle entrainment. A hydrocyclone is an efficient technology for a heterogeneous separation system owing to its great advantages of a simple structure, low energy consumption, large capacity, and flexible operating conditions. It has been applied in many areas, such as soil cleaning and remediation [39–42], hazardous materials removal [43,44], and wastewater treatment [45,46]. Strengthened by the vortex field, the hydrocyclone can be successfully applied for fast separation of very small particles. However, hydrocyclones are seldom used for desulfurization. In fact, if the adsorption is fast enough to be comparable to the separation speed of the hydrocyclone process, the combination of adsorption and separation simultaneously in one hydrocyclone system would provide a novel approach for efficient desulfurization.

Here, we used MOF-199 as the adsorbent and two-stage hydrocyclones as a simultaneous adsorption-separation device to achieve fast deep desulfurization. The typical organic sulfur of DBT dissolved in dodecane was selected as the model fuel. After studying the DBT-adsorption dynamics of MOF-199, we further investigated the separation efficiency by optimizing the operating conditions, including the dosage of MOF-199, the split ratio, and the inlet flow rate. Finally, fast, deep desulfurization was realized in this hydrocyclone-system through simultaneous adsorption-separation.

2. Experimental

2.1. Model fuel

Dibenzothiophene (DBT, $\text{C}_{12}\text{H}_8\text{S}$, with the molecular weight of 184.26), a typical organic sulfur compound in fossil fuels, was chosen as the representative of target organic sulfur compound. The model fuel for ADS was prepared by dissolving DBT (>98%) in dodecane (>98.5%) with given concentrations. The concentrations of DBT in the model fuel before and after the desulfurization were determined by the gas chromatograph equipped with a HP-5 capillary column (15 m \times 0.53 mm \times 1.5 μm film thickness) and a flame photometric (FPD) detector (GC-950, Haixin Chromatography).

2.2. Synthesis of adsorbent MOF-199

The adsorbents with larger mean particle size could be separated by hydrocyclones more efficiently. Herein, the size of mass-production of MOF-199 was well controlled and synthesized based on a modification of synthesis procedure reported by Xin et al. [47] Typically, 5.2 kg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (>99%) and 2.5 kg 1,3,5-Benzenetricarboxylic acid (H_3BTC , >98%) were dissolved in 60 L mixed solvent which is made of equal amount of N,N-dimethyl formamide (DMF, >99.5%), ethanol (>99.7%) and water at 80 $^\circ\text{C}$ for 24 h. The yield was higher than 90%. MOF-199 powders were activated at 160 $^\circ\text{C}$ under vacuum before use.

2.3. Characterization of MOF-199

The X-ray diffraction (XRD) patterns of MOF-199 was collected in the scan range of 2θ from 5 $^\circ$ to 40 $^\circ$ with a scan step of 0.02 $^\circ$ on a D/Max2550 VB/PC spectrometer using Cu K α radiation (40 kV and 200 mA). The textural properties of MOF-199 was determined from the nitrogen adsorption-desorption isotherms at 77 K on a Micrometrics ASAP 3020 sorption meter. The surface area was calculated by Brunauer-Emmett-Teller (BET) model. The granularity and shape of MOF-199 were tested with laser granularity analyzer (BT-9300Z) and scanning electronic microscope (SEM) by using a Nova Nano SEM 450. The pycnometer method was used for determining the skeletal density, which is the ratio of the mass to the volume occupied by the material excluding the volume of any open pores.

2.4. Adsorption dynamics of MOF-199

The adsorption dynamics of MOF-199 was studied by the batch experiment. In a typical experiment, 187.5 mg MOF-199 was added into 5 mL model fuel in a sealed glass bottle under stirring at 25 $^\circ\text{C}$ for a certain time. Then, the adsorbents were separated by the centrifugation. The concentrations of DBT in the model oil before and after the adsorption were determined by the gas chromatograph (GC, Haixin GC-950), equipped with a capillary column (HP-5, 15 m \times 0.53 mm \times 1.5 μm film thickness) and a flame photometric detector (FPD) detector. The amount of sulfur adsorbed was calculated by Eq. (1)

$$q_t = \frac{V}{M}(C_0 - C_i) \times \frac{M_{WA}}{M_{WS}} \quad (1)$$

where q_t is the amount of sulfur adsorbed on the adsorbent (mg S g^{-1} adsorbent), V is the volume of the model oil (mL), M is the mass of the adsorbent used (g), M_{WA} is the molecular weight of DBT, M_{WS} is the molecular weight of sulfur, and C_0 and C_i (mg S L^{-1}) are the concentrations of DBT in the model oil before and after the adsorption, respectively.

The pseudo second-order rate law was used to fit the adsorption dynamic data, which can be described as Eq. (2)

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