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Note from the field

Using activated clay for adsorption of sulfone compounds in diesel

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ABSTRACT

The aim of this study was to evaluate the adsorption performance of activated clay (bentonite) in removing sulfur compounds from diesel fuel. Studies have proved that oxidative desulfurization is more cost effective than the traditional hydrodesulfurization process. In this investigation, oxidative desulfurization was used under mild conditions with hydrogen peroxide as an oxidant, phosphotungstic acid as a catalyst and tetraoctylammonium bromide as a phase transfer agent, to convert sulfur-containing compounds in diesel to their sulfone forms. The sulfone compounds were then removed by adsorption using activated clay as an adsorbent. The performance of activated clay particles in adsorbing sulfone compounds was evaluated through equilibrium and kinetic studies. The adsorption kinetics was pseudo-second order. The initial sulfur content of 1109.3 ppm was reduced to below 10 ppm, achieving a sulfur removal rate of 99%. Therefore, activated clay was found to be effective in obtaining ultra-low sulfur diesel.

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1. Introduction

The burning of diesel fuel emits harmful SO_x (Stanislaus et al., 2010). The traditional desulfurization technique for removing sulfur from diesel is hydrodesulfurization (HDS), but the HDS process requires the use of hydrogen and extreme conditions of high pressure and high temperature (Bordoloi et al., 2014). However, oxidative desulfurization (ODS) has been found to be more cost-effective and efficient than HDS in oxidizing refractory compounds, especially 4,6-disubstituted DBT (Feng, 2010; Zhang et al., 2009; Zhou et al., 2009).

ODS involves two main reactions, which are the oxidation of sulfur compounds and the removal of their oxidation products, respectively. The oxidants that are typically used in ODS because they yield the best results are peroxides, such as hydrogen peroxide and tert-butyl hydroperoxide, utilized with heterogeneous catalysts (Bakar et al., 2012). Other studies have revealed that this oxidation process can be promoted using shear reactor instead of magnetic stirring and ultrasound (Chen et al., 2012; Duarte et al.,

2011; Fox et al., 2011). Second, the formed sulfone, which has different physical and chemical properties from those of fuel oil hydrocarbons, is removed using conventional separation techniques such as distillation, solvent extraction, adsorption, and decomposition (Alhamed and Bamufleh, 2009).

Adsorption of sulfone onto activated clay is a physical and chemical process wherein the pollutants adhere to the surfaces of adsorbents. The adsorbents were carefully selected for their high porosity, high adsorption efficiency, and high selectivity. One cheap material used as an industrial adsorbent is activated clay. Clays have the groups of microcrystalline minerals containing silicon, aluminum oxides, and hydroxides (Hameed, 2007). Some literatures have reported the uses of clays for the removal of 2,4,6-trichlorophenol, chromium IV ions, methylene blue, copper II ions, organic sulfur compounds, and hydrocarbons (Hameed, 2007; Li et al., 2012; Ugochukwu et al., 2014). In this study, therefore, the activated clay, namely bentonite, was used to study the removal of sulfone from oxidized diesel by adsorption.

2. Materials and method

All the chemicals listed in Table 1 with purity and sources were purchased commercially and used without further treatment.

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Table 1
Materials and chemicals list.

Materials	Source and concentration
Diesel	Taichin Global Company – sulfur 1109.3 ppm
Hydrogen peroxide (H ₂ O ₂)	Merck – 50% concentration
Phosphotungstic acid (PTA)	Merck – 98% purity
Tetraoctylammonium bromide (TOAB)	Merck – 98% purity
Activated clay	Ying-yue Resources Co., Ltd – powder form The chemical materials were included: SiO ₂ 70.40% Al ₂ O ₃ 15.71% Fe ₂ O ₃ 3.15% CaO 1.17% MgO 2.13% Na ₂ O + K ₂ O 1.43% H ₂ O 6.89%

2.1. Oxidation of diesel

Diesel fuel (1109.3 ppm S) was mixed for 30 min with H₂O₂ (50%, Merck), phosphotungstic acid (HPW) (98%, Merck), and tetraoctylammonium bromide (TOAB) (98%, Merck) in a high-shear mixer (IKA Ultra Turrax T25 digital) that was set at 15,000 rpm. The equipment was maintained at 343 ± 2 K using a water bath. The mixture comprised diesel: H₂O₂ in a 1:1 ratio, and 0.4 g of HPW, 100 mL diesel and 0.8 g of TOAB.

2.2. Batch adsorption process

Activated clay purchased from Ying-Yue Resources Co., Ltd. was used to remove sulfur from the oxidized diesel without further treatment. Equilibrium data were obtained by changing the amount of adsorbent from 1 to 10 g with a contact time of 90 min. All adsorption processes were observed at four temperatures (303–363 K).

2.3. Sulfur concentration analysis

In all experiments, the total sulfur concentration of the samples before and after the application of ODS was determined using SLFA 2100 Horiba. SLFA 2100 Horiba is fast and accurate because it uses X-ray fluorescence technique and can be utilized with the ASTM D4294 method.

3. Result and discussion

3.1. Characterization of activated clay

Effective adsorbents have a porous structure and favorable surface chemistry (Yu et al., 2013). Determining the surface area and morphology of an adsorbent is important. In this study, a Brunauer Emmett Teller (BET) analyzer was used to determine the pore size and surface area of fresh activated clay. The results of the analysis in Table 2 confirmed that the porous activated clay has a

Table 2
BET analysis of activated clay.

Parameter	Activated clay
Specific surface area (m ² /g)	158.46
Maximum pore volume (cm ³ /g)	8.10
Micropore volume (cm ³ /g)	0.244
Median pore diameter (nm)	7.566

median pore diameter of 7.566 nm. Its specific surface area is 158.46 m²/g, which this is almost twice that of thermal and acidified bentonite (Toor and Jin, 2012).

3.2. Controlled experiments

Equation (1) was used where C₀ and C_t refer to sulfur concentrations at t₀ (t = 0) and t_e (t = equilibrium) (Hameed, 2007). Using the total sulfur analyzer, both initial and equilibrium concentrations of sulfur in diesel were readily available.

$$\text{Sulfur Removal Rate (\%)} = 100 \times (C_0 - C_t)/C_0 \quad (1)$$

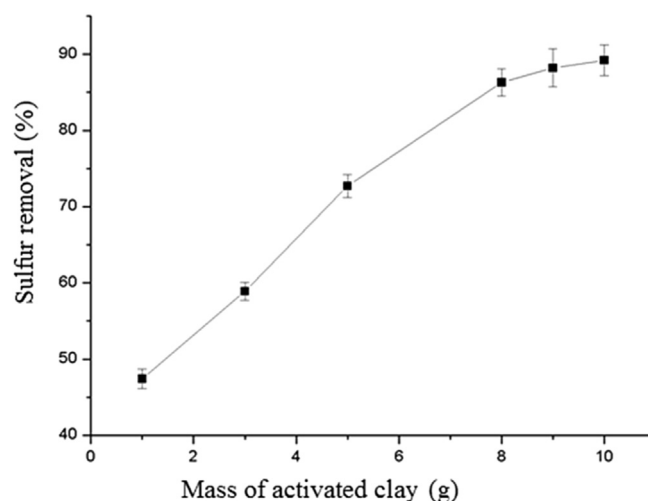
Removal of sulfur was observed in both the oxidation and the adsorption processes. For the removal of sulfur oxidation, the C₀ and C_t values were obtained from the sulfur content of untreated diesel (t = 0) and oxidized diesel, respectively. Diesel was oxidized for 30 min. Therefore, C_t was obtained after 30 min. The initial concentration of sulfur in diesel was 1109.3 ppm. After phase separation in the oxidation process, the sulfur content had decreased to 804.2 ppm. Therefore, the initial sulfur concentration had been reduced by 27.5%.

3.3. Effect of activated clay at different dosage

Fig. 1 shows the sulfur adsorption efficiency in six different adsorbent dosages. It is observed that the increase in adsorbent dosage from 1 to 10 g results in an increase in sulfur removal efficiency from 47.4 ± 1.3 to $89.2 \pm 2\%$. Past adsorption studies reported that increase in adsorbent dosage was due to increased surface area and adsorption sites for adsorbate to adhere to (Özer and Dursun, 2007; Öztürk and Kavak, 2005; Thinakaran et al., 2008). The same effect was observed when dosage was increased. This confirmed that increasing activated clay provided more surface area and adsorption sites for sulfone to adhere to, resulting in an increase in sulfur removal rate. The dosage with highest removal rate was 10 g and this was used in the succeeding experiments.

3.4. Effect of agitation speed

Agitation speed is an important parameter in adsorption because it affects the diffusion of solutes in the bulk solution and the development of the external boundary film (Crini and Badot,

**Fig. 1.** Adsorption efficiency of activated clay at different dosages (agitation rate = 300 rpm, T = 303 K).

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