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Adsorption of sulfur compound utilizing rice husk ash modified with niobium

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ABSTRACT

Adsorbents based in rice husk ash (RHA) modified with niobium pentoxide were prepared for impregnation methods and applied in sulfur removal in liquid fuels. The solids were characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy, nitrogen physisorption and thermal analysis; they show that there was no qualitative change in the amorphous structure of the RHA; however, the method of impregnation could modify the particle size and topology of RHA particles. The larger sulfur removal (>50%) was achieved using RHA with 5 wt.% Nb_2O_5 at a dosage of 10 g L^{-1}, after 4 h of contact with the model fuel. The kinetic study of adsorption of thiophene showed that the models of pseudo-second order and intra-particle diffusion best fit the experimental data. The adsorption experiments with the thiophenic derivatives compounds show a large selectivity of the adsorbent.

1. Introduction

The hydrodesulfurization (HDS) is the traditional method for handling liquid fuels during the sulfur removal. However, increasing regulatory requirements to reduce the concentration of sulfur compounds (<10 ppm) on liquid fuel results in high cost for the HDS technique [1,2]. The desulfurization by adsorption process is a promising alternative, because it is a procedure that operates under milder conditions than the conventional HDS, without compromising the quality of fuel, and it is also able to reduce the final cost of operation [1–4].

For more than a decade, a wide variety of compounds used to obtain adsorbent is present in desulfurization studies by adsorption [5–8], and silica is one of the main materials used in this type of study [5–9]. In nature, silica is well known for its incorporation in the structure of certain plants [10]. For example, rice assimilates the orthosilicic acid contained in the soil's water, which is polymerized to form the amorphous silica of the grain husks [10–12]. During rice processing, the rice husk (RH) becomes a farming industry waste that can be used to replace the wood used in boilers [12,13]. The burning process of the RH in boilers results in the generation of another residue, the rice husk ash (RHA), which leads to serious environmental problems. When this powder – containing constituents silica – is disposed without precautions it brings serious risks to the environment and human health [12,14,15]. In 2007 alone, Brazil generated around 440,000 tons of RHA [16,17].

RHA is an excellent source for obtaining silica in which can be obtained with about 92 wt.% purity [12,13,18–21]. In addition, the use of RHA has also been investigated in obtaining adsorbents and catalysts. For example, RHA has been applied as an adsorbent for removal of metal ions [22,23] and dyes [23,24], and the adsorption of organic compounds such as α-picoline [25] and pyridine [26]. Similarly, it was used as a support for preparing nickel based catalysts in catalytic reactions such as CO and CO_2 methanation and hydrogenation of unsaturated oils [12,27]. Considering the fact that the adsorbent materials most used in desulfurization have a relatively high cost, the use of an unconventional adsorbent based on rice husk ash (RHA), for example, could reduce the costs of the process.

The incorporation of metals such as Cu, Ni, Zn, Ag, Ce and Co [1,2,28,29] in the form of exchangeable cations, or in the form of

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oxides such as Al_2O_3 and TiO_2 [30–34], has received attention in desulfurization by adsorption, because of several possible interactions as much both the aromatic rings as with the heteroatom of sulfur (in the thiophenic derivatives), providing a greater selectivity for the sulfur compounds [35]. For example, the theoretical and experimental study of titanium oxide in the adsorption of thiophene demonstrated relatively weak and selective interactions between thiophene molecules and the metal oxide [36]. In previous work of our research group [37], it was observed that the adsorbents prepared from ZSM-5 had their adsorption capacity of thiophene potentialized when this material is impregnated with niobium pentoxide. According to Hüger et al. [38], elemental sulfur has a significant interaction with metallic niobium. All this makes attractive the use of metal oxides (in this case the niobium oxide) for the synthesis of adsorbents for desulfurization.

In this sense, we investigated the new compound RHA adsorbent impregnated with niobium pentoxide in the adsorption of sulfur in model fuels considering the concentration of the supported material, the effect of the adsorbent dosage, temperature, contact time and the different types of organosulfur compounds existing in the fuels. Therefore, the study of the conditions and mechanism of the adsorption process is very important for the combination of mathematical models that help predict the behavior of the adsorbent under any reaction conditions, simulating real liquid fuels.

Thus, the present work studied the adsorption of thiophene and derivatives using adsorbents based on RHA in order to identify the best operating conditions for the removal of sulfur from liquid fuels.

2. Materials and methods

2.1. Materials

To prepare the adsorbent materials we used rice husk obtained in the city of Barreira/BA, Brazil and niobium ammonium oxalate complex – $NH_4[NbO(C_2O_4)_2(H_2O)_2](H_2O)_n$ – supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM), now being referred to as NbAOC. The model fuels were prepared from 2,2,4-trimethylpentane (Dinâmica, UV/HPLC grade), thiophene (Sigma–Aldrich, ≥99%), benzothiophene (TCI America, CG grade) and dibenzothiophene (TCI America, CG grade).

2.2. Adsorbent and model fuel preparation

The adsorbents were prepared by incipient wetness impregnation and wet impregnation methods using NbAOC as the precursor of niobium. In the incipient wetness impregnation, a solid mixture of RHA and NbAOC was humidified with distilled water and left to stand for 24 h in a desiccator. The adsorbents (called Nb(x)RHAI) containing from 2 to 15 wt.% Nb_2O_5 (x = 2, 5, 10 and 15% of Nb_2O_5) were dried at 120 °C/2 h, calcined at 300 °C/6 h (10 °C min^{-1}), and activated at 300 °C/30 min (10 °C min^{-1}). In the wet impregnation, distilled water was added to a similar solid mixture of RHA/NbAOC in proportion of 10 mL g^{-1}. The mixture was kept in a flask and heated with stirring at 80 °C until complete evaporation of the water. The adsorbents obtained (called Nb(x)RHAA) were dried, calcined at 300 °C/6 h (10 °C min^{-1}), and activated at 300 °C/30 min (10 °C min^{-1}).

The model fuels were prepared from dilution of thiophene, benzothiophene and dibenzothiophene in 2,2,4-trimethylpentane at initial concentrations of sulfur (C_0) close to 650 mg L^{-1}. Moreover, binary solutions were also prepared of thiophene–benzothiophene (T–BT), thiophene–dibenzothiophene (T–DBT) and benzothiophene–dibenzothiophene (BT–DBT) in 1:1 ratio between the different types of organosulfur molecules and maintaining the C_0 total of sulfur around of 650 mg L^{-1}.

2.3. Adsorbent characterization

2.3.1. X-ray diffraction (XRD) and scanning electronic microscopy (SEM)

The diffraction powders were obtained with a Shimadzu equipment (XRD-6000), utilizing the Kα line of cupper (CuKα) at 40 kV and 30 mA. The scanning interval utilized was 2θ/5–60°, at a scanning speed of 2° min^{-1}. The SEM images of the samples were obtained on the Quanta 250 equipment (FEI Company) in an acceleration of 20–30 kV with gold coating treatment. The analysis was performed at the Mineralogical Laboratory Techniques of the Department of Geosciences in the Federal University of Amazonas (UFAM).

2.3.2. Thermogravimetric analysis, infrared spectroscopy and N_2 adsorption

Thermogravimetric analysis was obtained from TA Instruments SDT 2960 Simultaneous equipment from room temperature to 1000 °C (10° C min^{-1}) at flow rate 100 mL min^{-1} of synthetic air. The N_2 adsorption isotherms were obtained at the ASAP 2020 device from Micromeritics, with a degas treatment of 250 °C for 2 h under vacuum. The infrared spectroscopy analysis was performed using Nicolet 6700 FT-IR equipment (Thermo Scientific) with a resolution of 4 cm^{-1} and 256 scans in the region of 400–4000 cm^{-1}. The samples were diluted 1:100 in KBr, dried, and pressed. All analysis was conducted at the Laboratório de Catálise (LabCat) at the Institute of Chemistry (IQ) of the University of Brasilia (UnB).

2.4. Sulfur adsorption procedure

For the study of the factors that affect the adsorption of sulfur in the fuel model, we evaluated the effects of Nb_2O_5 content and dosage of adsorbent. The sulfur adsorption tests were performed in a reflux system under strong stirring and under heating at 80 °C/4 h, keeping the concentration of the adsorbent in the fuel equal to 10 g L^{-1}. In these tests we used different materials containing niobium pentoxide. The effect of time and temperature was evaluated, ranging time of 10–240 min, and the temperature between 28 at 80 °C. The effect of the concentration of the adsorbent was evaluated by varying the amount of adsorbent between 8 and 20 g L^{-1} in solution, maintaining the same conditions for the effect of time and temperature analysis.

After the adsorption test, the synthetic fuel was separated from the adsorbent by vacuum filtration. The filtrate was analyzed in a X-ray fluorescence spectrometer (XRF) RayNy EDX-700 model (Shimadzu) under 15 kV voltage, scan time of 100 s, atmosphere of air and in liquid mode. For calculation of the amount adsorbed and sulfur removal we used the following equations:

$$q_t = \frac{V(C_0 - C_t)}{W} \qquad (1)$$

$$\text{Sulfur removal (\%)} = \frac{(C_0 - C_t)}{C_0} 100 \qquad (2)$$

where q_t is the amount adsorbed at time t (mg g^{-1}); C_0 is the initial concentration of sulfur (mg L^{-1}); C_t is the sulfur concentration at time t (mg L^{-1}); V is the model fuel volume (L); and W the mass of adsorbent added to the model fuel (g).

2.5. Kinetic study of sulfur adsorption

The kinetic models tested (Table 1) refer to theories of chemisorption and diffusion phenomena [22,39–46], which describe the solid–liquid interaction. K_1 is the rate constant for pseudo first order (min^{-1}); q_e is the amount adsorbed at equilibrium (mg g^{-1}); t is the time (min); q_t the amount adsorbed at