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Full Length Article

Adsorptive desulfurization of metal phthalocyanine functionalized poly-ionic liquids grafted to silica gel

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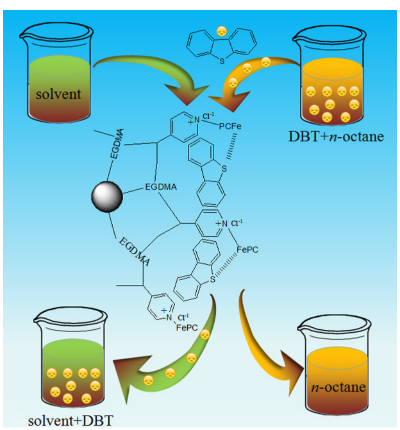
GRAPHICAL ABSTRACT

Metal phthalocyanine functionalized poly-ionic liquids grafted to silica gel were synthesized for adsorptive desulfurization of dibenzothiophene as adsorbent. Their performance of adsorptive desulfurization at room temperature and atmospheric pressure was better than other reported adsorbents. the regeneration of adsorbents doesn't need burning, and only need washing by solvent, the solvent can been recycled and reused by rectification. There aren't secondary pollution.



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ABSTRACT

Four metal phthalocyanines (Pc-4, 8, 12, 16) functionalized ionic liquids were polymerized on the surface of silica gel as adsorbent materials. They were characterized by FT-IR, BET, SEM and TEM measurements. The characterization results proved that the adsorbents were prepared successfully. Their adsorptive desulfurization performances to dibenzothiophene in model oil at room temperature and atmospheric pressure were investigated in detail. The results showed that the adsorptive desulfurization effect of P-4 was best. The optimal amount of adsorbent was 10 g/100 mL model oil. The maximum amount of DBT adsorbed was 52.41 mg/g, superior to some previously reported adsorbents. The adsorption equilibrium and kinetics of this adsorbent were also examined. The adsorption behavior fitted well to Freundlich isotherm model, pseudo-second-order kinetics model and Weber and Morris kinetics model. Adsorption and regeneration by solvent processes were performed 10 times, and the adsorption capacity of the adsorbent did not decrease obviously. P-4 also had a good adsorption effect on different sulfur compounds, and the order of removal was DBT > BT > 2-MTH > TH.

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1. Introduction

In recent years, haze has become a more frequent and serious problem in China, threatening human health. This problem has received increasing attention from the government and citizens of China [1]. haze has become a worldwide phenomenon because of its serious environmental and health effects [2]. The effluent gases from the combustion of coal for power generator and exhaust gas emissions from increasing vehicle transportation have been proven to be major factors for the production of haze in most developing countries in the world [3]. The sulfur compounds in automobile exhaust and effluent gases can cause acid rain and environmental pollution. In addition, sulfur compounds in fuel oil cause pollution during the operation of three-way catalysts in vehicle catalytic converters [4]. The traditional hydrodesulfurization (HDS) technology already cannot accomplish deep desulfurization (15 ppm). Therefore, the deep desulfurization of gasoline or diesel oil has become a serious challenge with growing environmental concern. Alternative desulfurization processes that operate under moderate conditions have been developed and extensively investigated, such as oxidative desulfurization (ODS), biodesulfurization, extractive desulfurization (EDS), extraction coupling with oxidative desulfurization (ECODS) and adsorptive desulfurization (ADS) [5–9].

Adsorptive desulfurization can occur at room temperature and pressure. Therefore, adsorption desulfurization has been investigated by an increasing number of researchers [10]. The reported adsorbents include activated carbons, mesoporous materials, zeolites, alumina, cyclodextrin, and metal-organic frameworks (MOFs) [11–19]. However, the sulfur capacities of these adsorbents are not ideal. Currently, research is focused on finding reliable, cost-effective, high sulfur capacity and high activity adsorbent materials.

Ionic liquids (ILs) have been developed rapidly as extraction agents for EDS and ECODS because ILs have aromatic structures and show outstanding sulfur extracting ability owing to the p-complexation between ILs and aromatic sulfides [20]. However, these materials are difficult to apply in industrial application because of their disadvantages, such as high cost, high viscosity and recycling difficulty [21]. To overcome these shortcomings, a method of loading ILs on support materials was deemed effectively [22,23] The reported support materials include silica [24], magnetic nanoparticles [25], mesoporous silica [26] and polymers [27]. However, the catalytic activities of these supported ILs cannot withstand recycling. The acid sites of ILs on the support are removed easily from the surface after completion of the reaction [28]. Recently, poly-ionic liquids (PILs) made from ionic liquid monomers have gained attention from researchers because of their potential applications. Extensive application fields have been reported, for example, gas separation materials [29,30], electrolyte materials [31], catalyst [32], polymer electrolytes [33], and ionic conductive materials [34]. However, few papers have reported on the use of a PIL as an adsorbent in adsorptive desulfurization.

Therefore, in this study, we aimed to study the efficiency of PILs grafted onto silica gel (PILs/SiO_2) for the adsorption removal of dibenzothiophene (DBT). This work investigated the synthesis and characterization of PILs, and the optimization of the adsorptive properties of PILs. The adsorption kinetics and equilibrium of DBT on the PIL/SiO_2 materials were examined, and the equilibrium and kinetics data were processed.

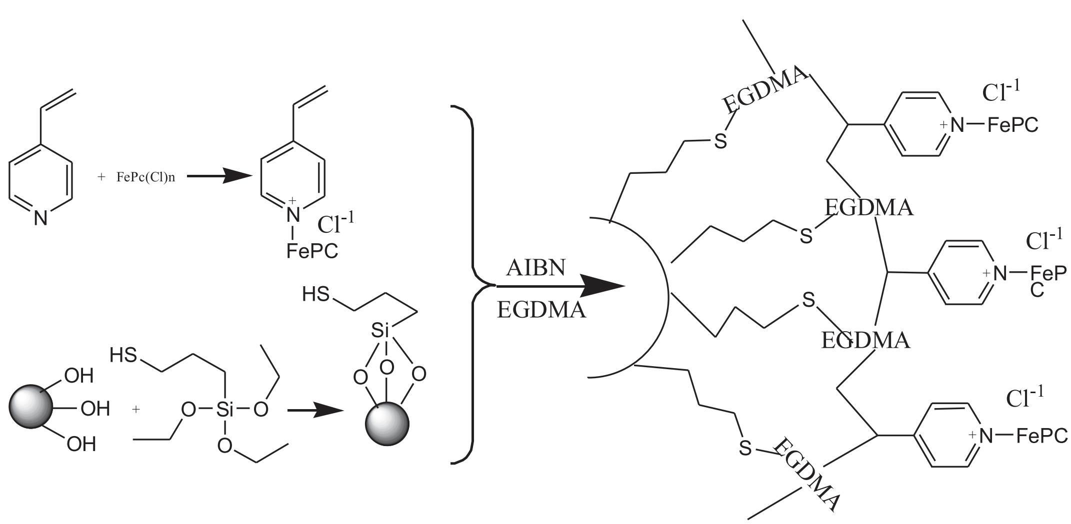
2. Materials and methods

2.1. Materials

Tetrachlorophthalic anhydride ($C_8Cl_4O_3$, 99%), pyromellitic dianhydride ($C_{10}H_2O_6$, 99%), diaminomethanal (CH_4N_2O), ammonium molybdate ($H_8MoN_2O_4$), $FeCl_3$(CR), 4-vinylpyridin (C_7H_7N), triethoxyvinylsilane ($C_8H_{18}O_3Si$,97%), dibenzothiophene ($C_{12}H_8S$, 98%), *n*-octane (C_8H_8, 99%), and 2,2-azobisisobutyronitrile ($C_8H_{12}N_4$, AIBN, 99%) were purchased from ALADDIN-E.com. Solvents (methanol, ethanol and etc.) were obtained from Tianjin Chemical Reagent Co. Ltd. Silica gel was purchased from Qingdao Haiyang Chemical Co. Ltd.

2.2. Preparation of the adsorbents

Iron phthalocyanine ($FePc(Cl)_n$ (n = 4, 8, 12, 16)) was prepared by the microwave method described in our previous paper [35]. Then, a mixture of 10 g of $FePc(Cl)_n$, 1.5 g of 4-vinylpyridine (molar ratio = 1:1) and 50 mL of DMSO were added to a 250 mL three-necked, round-bottomed flask and stirred for 24 h at 80 °C. Then, solution A was obtained. Silica gel (20 g, particle size: 0.85–2.0 mm, 0.60–0.95 mm or 0.42–0.60 mm), 10 mL of triethoxyvinylsilane and 50 mL of ethanol were poured into a 250 mL three-necked, round-bottomed flask and stirred for 8 h at 80 °C with reflux. Then, the modified silica gel was filtered, washed and dried. The modified silica gel (approximately 23 g) and 0.01 g of AIBN were added to solution A, and this mixture was stirred for 8 h at 80 °C under a nitrogen atmosphere. Finally, black green silica gel (P-VpFePcCl$_n$/SiO_2, n = 4, 8, 12, 16) was obtained, which was filtered, washed, dried and kept in a desiccator. The simple preparation of P-VpFePcCl$_n$/SiO_2 (n = 4, 8, 12, 16) is outlined in Scheme 1, and the gels are named P-4, P-8, P-12 and P-16, respectively.



Scheme 1. Synthesis process of P-4, P-8, P-12 and P-16.