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Selective removal of benzothiophene and dibenzothiophene from gasoline using double-template molecularly imprinted polymers on the surface of carbon microspheres

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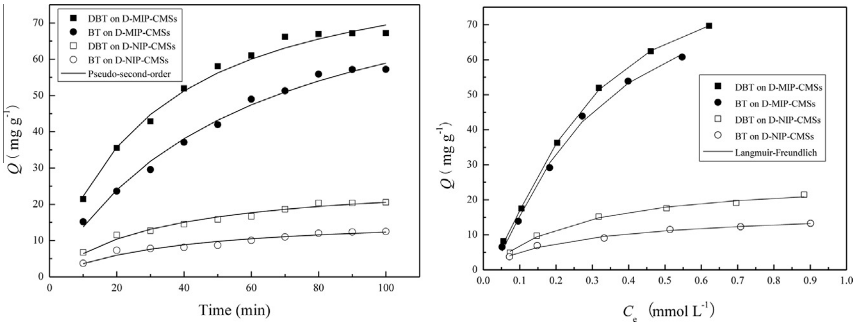
HIGHLIGHTS

- Novel double-template molecularly imprinted materials D-MIP/CMSs were prepared.
- The D-MIP/CMSs have good selectivity for benzothiophene and dibenzothiophene.
- The D-MIP/CMSs can be used for quickly removing benzothiophenes in fuel oil.
- Computer simulation was used for confirming the experimental results.

GRAPHICAL ABSTRACT

Novel double-template surface molecularly imprinted carbon microspheres were synthesized by using benzothiophene and dibenzothiophene as template molecules, which offer high binding capacity and selectivity for removal of sulfur-containing compounds from model fuel oil.



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ABSTRACT

A novel double-template molecularly imprinted polymer (D-MIP) on the surface of carbon microspheres (CMSs), using benzothiophene (BT) and dibenzothiophene (DBT) as the template molecules, was prepared for the removal of benzothiophene sulfides from fuel gasoline. Field emission scanning electron microscopy and Fourier Transformation Infrared Spectrometry were used to characterize the morphology and structure of the D-MIP/CMSs. The adsorption behaviors of the D-MIP/CMSs including adsorption kinetics, isotherms, selectivity and regeneration were detected in detail by gas chromatography. The D-MIP/CMSs exhibited excellent selectivity toward BT and DBT with higher binding capacity in simulated gasoline compared to non-imprinted polymer (D-NIP/CMSs). The adsorption equilibrium of D-MIP/CMSs was achieved within 90 min and the adsorption capacity reached 57.16 (BT) and 67.19 mg g^{-1} (DBT), respectively. The pseudo-second order model and Langmuir–Freundlich isotherm described the adsorption of benzothiophene sulfides on the D-MIP/CMSs well. The D-MIP/CMSs could be used 10 times without significant loss in adsorption capacity. In addition, the D-MIP/CMSs exhibited good desulfurization effect in real oil. The D-MIP/CMSs provides a new material for deep desulfurization of fuel oils.

1. Introduction

Benzothiophenes are important organosulphur compounds mostly found in gasoline and diesel. The difficulty in removing

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them because of their steric hindrance has become a challenge in desulfurization investigations [1,2]. These organosulphur compounds, when burned, produce sulfur dioxide which is not only a major source of acid rain, but also the reason for equipment corrosion and catalyst poisoning. Additionally, people with asthma, emphysema, and other pulmonary diseases are most deleteriously affected by sulfur compound pollutants. As an alternative and complementary method for deep desulfurization, the molecular imprinting technique, which offers a simple way to remove the refractory sulfur compounds under mild conditions, has attracted considerable attention [3–7].

Molecular imprinting is a powerful synthesis method for creation of specific binding sites in molecularly imprinted polymer (MIP), which can effectively recognize specific adsorbates in the adsorption process as a result of the high affinity and selectivity towards the templates [8,9]. In this preparation process, functional monomer and cross-linking agent are co-polymerized in the presence of template. After the removal of the template, MIP is obtained with the formation of imprinted recognition sites and cavities complementary to the shape, size and functionality of the template. Because of the predetermined specificity, MIP has potential applications in affinity-based separations, biomimetic sensors and assays. Haupt and Mosbach [7] found MIP can be extended further to find increasing applications. Castro et al. [6] used dibenzothiophene sulfone (DBTS) as template for the preparation of MIP. The obtained MIP showed better binding of DBTS than non-imprinted controls, and was also superior in adsorption of organosulphur compounds such as the maximum adsorption of dibenzothiophene (DBT) and benzothiophene (BT) present in a model mixture. However, the conventional bulk MIP has intrinsic limitations, such as low adsorption capacity, poor site accessibility and irregular shape [10]. To overcome the defects, surface molecular imprinting technique has been proposed [11–13]. That is, MIP is prepared by generating binding sites on the surface of solid substrates [14,15]. At present, some MIP based on various functional materials, such as SiO_2, TiO_2 [16] and carbon nanotubes, have been reported for deep desulfurization. Hu et al. [17] synthesized the imprinted polymer for the selective BT recognition on the surface of SiO_2, which was chemically modified with γ-aminopropyltriethoxysilane by using methacrylic acid (MAA) as the functional monomer, ethylene glycol dimethacrylate (EDMA) as the crosslinker, and BT as the template molecule. The adsorption capacity of the imprinted polymer for BT reached 57.4 mg g^{-1}, exhibiting good specific BT recognition. Xu et al. [18] prepared the molecularly imprinted polymer composites, using DBT as the template, 4-vinylpyridine as the functional monomer and tetratitanate whisker ($K_2Ti_4O_9$) as the carrier. The MIP/$K_2Ti_4O_9$ exhibited recognition capacity (~30 mg g^{-1} at 45 °C) and binding affinity for DBT.

An efficient imprinted adsorbent should consist of a stable and insoluble matrix. Carbon microspheres (CMSs) are ideal support materials because of their stability under acidic conditions, large surface and good mechanical stability [19]. Up to now, CMSs have been used as carrier for preparing MIP. Yang et al. [20] obtained the molecularly imprinted materials on the surface of CMSs modified by acid treatment and silylation, using DBT as the template, MAA as the functional monomer, EDMA as the cross-linking agent and azodiisobutyronitrile as the initiator through in situ polymerization. The static adsorption results show that the adsorption equilibrium time was about 5 h and the equilibrium adsorption amount was 109.63 mg g^{-1}. In addition, Yang et al. [21] attempted the synthesis of MIP/CMSs by grafting-polymerization. The macromolecule poly-2-acrylamido-2-methyl propanesulfonic acid was grafted firstly on the surface of CMSs, then, with DBT as the template, MIP was synthesized for adsorbing DBT. In dynamic adsorption, the saturated adsorption amount was 2.54 mg g^{-1}. In our previous work, CMSs-supported molecularly imprinted polymer MIP/CMSs for DBT selectively removing was prepared and the maximal adsorption amount was 88.83 mg g^{-1} in the simulated oil (the solution of n-hexane with 225 ppm DBT) [22]. After adsorbed by MIP/CMSs, the content of DBT decreased significantly from 225 to 62 ppm in 180 min and the removal degree reached 72.4%. It is suggested that the MIP formed on the surface of CMSs exhibited good desulfurization capacity. However, the MIP in these researches was prepared using single template molecule and sometimes did not exhibit high affinity and selectivity for other organosulfur compounds in gasoline and diesel. To overcome the limitation, using MIP prepared with more than one compound as templates to simultaneously remove the organosulfur compounds in a group from fuel oil is proposed. Simultaneously, it is economical to remove a group of pollutants together rather than remove a single pollutant [23].

In this research, a novel double-template molecularly imprinted polymer (D-MIP) on the surface of CMSs using BT and DBT as the template molecules was synthesized. Compared with the previous work, the most important innovation of this research is the use of multiple organosulfur compounds as templates to synthesize MIP. Thus, the multi-imprinted MIP can remove a group of organosulfur pollutants simultaneously from fuel oil. The versatility and feasibility guarantee the easier and faster reduction of total sulfur content. The adsorption properties of the resulting D-MIP/CMSs including kinetics, isotherms, selectivity, dynamic adsorption, regeneration and removing of templates in the real oil have been discussed in detail. The association between the functional monomer and the template molecules has been further studied through computer simulation.

2. Experimental

2.1. Materials

CMSs (~350 nm in diameter) were synthesized by chemical vapor deposition using C_2H_2 as carbon source. H_2SO_4 and HNO_3 were obtained from Taiyuan Fertilizer Factory Chemical Reagent Factory, Taiyuan, China. P-(chloromethyl)phenyl-trimethoxy silane (CMTMS, 95%) was purchased from abcr GmbH & Co., KG, Germany. Sodium N,N-diethyldithiocarbamate trihydrate (NaDEDTC, ⩾99%) and indole (⩾99%) were obtained from Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. MAA (⩾99%) was supplied by Chemical Reagent Company of Tianjin University, Tianjin, China. EDMA (98%), BT (⩾98%), DBT (98%) and biphenyl (⩾99%) were purchased from Alfa Aesar China, Tianjin, China. Real oil (93# gasoline) was purchased from one gas station in Taiyuan, China. All other chemicals were of analytical grade. Deionized water was used to prepare all buffers and solutions.

2.2. Preparation of D-MIP/CMSs

(i) Modification of CMSs with iniferter. The iniferter was coupled onto the surface of CMSs in three steps with mixed acids, CMTMS and NaDEDTC. CMSs (0.5 g) were suspended in mixed acids solution (120 mL, 96 wt% H_2SO_4 and 65 wt% HNO_3 in volume ratio 3:1) and refluxed at 80 °C for 20 min under electromagnetic stirring. The treated CMSs were washed with deionized water to neutrality and then vacuum filtrated, dried at 50 °C overnight to give hydroxyl functionalized CMSs (oxidized CMSs). Then, benzyl chloride groups were introduced by the reaction of the oxidized CMSs-bound hydroxyl group with CMTMS. Oxidized CMSs (0.4 g) were added to toluene (25 mL) followed by the addition of CMTMS in concentrations of 5% (w/v, 0.5 g CMTMS in 10 mL toluene). The mixture was refluxed in N_2 atmosphere