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Preparation of molecularly imprinted polymer coated magnetic multi-walled carbon nanotubes for selective removal of dibenzothiophene

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ABSTRACT

Novel molecularly imprinted polymers (MIPs) on the surface of magnetic multi-walled carbon nanotubes (MMWCNTs) were prepared using dibenzothiophene (DBT) as template, methacrylic acid (MAA) as functional monomer, ethylene glycol dimethacrylate (EGDMA) as cross-linking agent and ammonium persulfate (APS) as initiator. The synthetic product was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Fourier transform infrared spectroscopy (FTIR). Batch mode adsorption studies were performed to evaluate the adsorption kinetics, adsorption isotherms, and selective recognition of MMWCNTs-MIP. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order equation. The pseudo-second-order exhibited the best fit for the kinetic studies (R^2= 0.9985), which indicates that chemisorption process limits adsorption of DBT. The adsorption equilibrium of DBT using MMWCNTs-MIP could be well-defined with the Langmuir isotherm model instead of the Freundlich isotherm model, and the maximum adsorption capacity was calculated as 47.8 mg g^{-1}. Compared with magnetic non-imprinted polymer (MNIP), magnetic MIP (MMIP) possessed a better adsorption property toward DBT, showing its potential for deep desulfurization.

1. Introduction

Molecular imprinting represents a new class of materials possessing high selectivity and affinity for the target molecule [1]. Molecularly imprinted polymers (MIPs) are prepared by formation of specific recognition sites in a polymeric matrix [2]. The functional monomers are mixed with the template molecules so they could bind covalently [3] or non-covalently [4]. Non-covalent interactions between the template and the functional monomers is probably the most flexible regarding the selection of the functional monomers and the possible template molecules [5]. The comparative advantages of the MIPs such as thermal and chemical stability, low cost, ease of preparation, repeated operations without loss of activity, high mechanical strength, and high selectivity and feasibility of miniaturization allow them to be effectively utilized in a wide range of fields, such as catalysis [6], chromatographic separation [7], solid-phase extraction (SPE) [8] and biosensor [9]. MIPs were usually synthesized by bulk polymerization. However, this method showed severe disadvantages such as low rebinding capacity, heterogeneous distribution of binding sites, incomplete imprinted molecules removal and low binding affinity to target molecule [10]. Surface molecularly imprinted technique is one of the important synthetic methods of MIP and has outstanding advantages (e.g. being simple, convenient to prepare, low mass-transfer resistance, high selectivity, high adsorption capacity) [11]. In surface imprinting, the shape of the MIPs will be determined by the support. Various surface imprinting techniques are carried out on a variety of substrates such as fibers [12, 13], silica particles [14, 15], graphene [16], multi-walled carbon nanotubes (MWCNTs) [17] and inorganic [18, 19].

An efficient imprinted adsorbent should consist of a stable and insoluble matrix. Nanomaterials, which benefit from unique advantages, indicate special physical and chemical properties [20, 21]. Among the nanomaterials, MWCNTs possess high porosity, large specific surface area, hollow structure, and light mass density [22], these properties reveal that they can be used for preparing

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reinforced polymer composites [23]. At present, magnetic molecularly imprinted polymers (MMIPs) can make separation process simple and fast, because it can be isolated easily from samples by using an external magnetic field without additional centrifugation or filtration step [24]. Recently, MMIPs have been prepared and applied in pollution removal [25, 26]. The resulting MMIPs are added to a sample solution containing the analyte and stirred to allow the analyte to adsorb onto the magnetic polymers. The magnetic polymers with captured analyte are then gathered from the suspension using a strong magnetic field. Finally, the target analyte is eluted from the magnetic polymers and analyzed.

The existence of organosulfur compounds in transportation fuels is not only a major source of acid rain, but also the reason many serious diseases of human respiratory system, such as lung cancer [27]. Accordingly, efficient removal of organosulfur compounds from diesel oil is an interesting research area [28, 29]. Recently, a variety of desulfurization technologies have achieved some success in removing the sulfur components in the fuel [30]. However, it is difficult to remove some refractory sulfur-contenting compounds such as benzothiophene (BT), dibenzothiophene (DBT) and their derivatives [31, 32]. As an alternative method for conventional deep desulfurization, the molecular imprinting technique, which offers a simple way to remove the refractory sulfur compounds such as DBT under mild conditions, has attracted considerable attention [33–35].

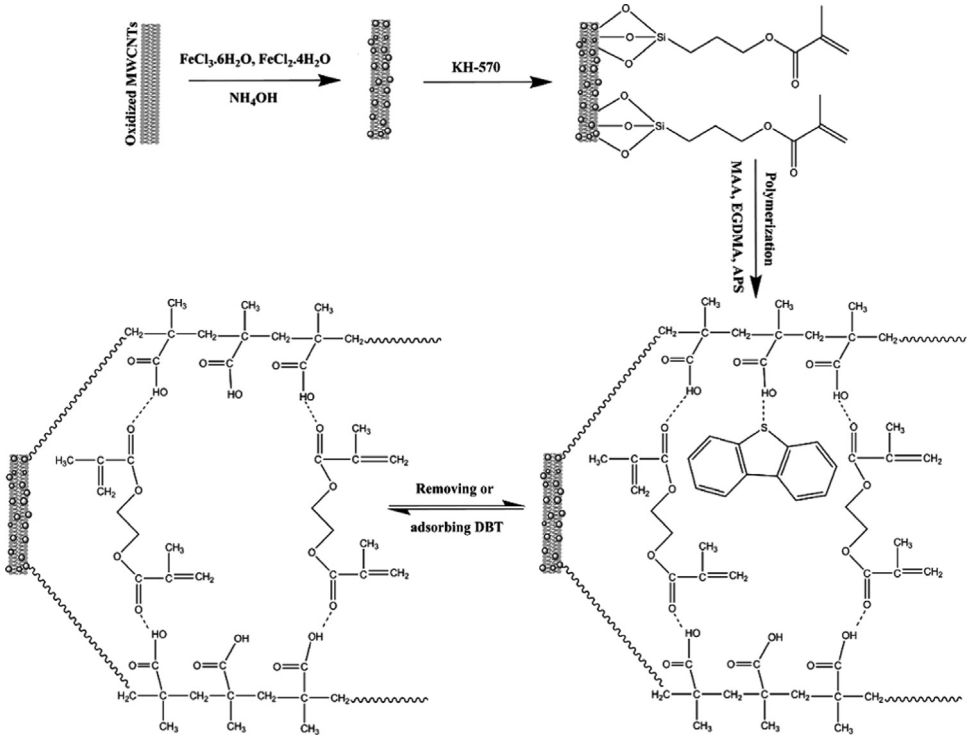
Nowadays, some MIPs based on various functional materials have been reported for deep desulfurization. Yang and co-workers [36] synthesized the imprinted polymer for selective separation of DBT on the surface of carbon microspheres (CMSs), which was modified with acid and silylation treatment by using methacrylic acid (MAA) as the functional monomer, ethylene glycol dimethacrylate (EDMA) as a cross-linking agent, azoisobutyronitrile (AIBN) as initiator and DBT as the template molecule. Xu et al. [37] fabricated a novel surface imprinted polymer composites (MIP/$K_2Ti_4O_9$) using DBT as the template, 4-vinylpyridine (4VP) as the functional monomer and potassium tetratitanate whisker ($K_2Ti_4O_9$) as the sacrificial support material. The adsorption capacity of the proposed imprinted polymer for DBT reached 55.5 mg g^{-1} at 25 °C, exhibiting high recognition selectivity and binding affinity to DBT. Core–shell Fe_3O_4@SiO_2 nanoparticles was also employed by Li et al. [38] as magnetic support for the selective adsorption and separation of DBT from oil solution. The research results of this work indicated that the selectivity recognition of MMIPs toward DBT was more than two times as high as the magnetic non-imprinted polymers (MNIPs).

However, no previous studies have been reported on the use of magnetic MWCNT (MMWCNT) as a new carrier for selective removal of DBT. Herein, we synthesized a novel MMIP by using MMWCNT composite as carrier and DBT as a template molecule. MAA and EGDMA were selected as a functional monomer and a cross-linker agent, respectively. The adsorption behavior of the synthesized MMIP to ward DBT was studied. The adsorption isotherms were determined and discussed. The whole synthesis route of the magnetic imprinted polymer is shown in Scheme 1.

2. Experimental

2.1. Reagents and materials

All reagents and chemicals used in the study were of analytical grade. DBT and 3–methacryloxypropyl trimethoxysilane (KH-570) were obtained from Sigma-Aldrich Chemical Company (St. Louis, MO, USA). MWCNTs (95% purity) with an average outer diameter of 5–20 nm, length of 1–10 μm, number of walls 3–15 and surface area of 350 m^2 g^{-1} were purchased from Palasmachem GmbH (Berlin, Germany). Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium hydroxide (NaOH), EGDMA, MAA and ammonium persulfate (APS) were supplied by Merck (Darmstadt, Germany). Acetonitrile, methanol, acetic acid chloroform were purchased from Merck.



Scheme 1. A schematic representation of preparation of MMWCNTs-MIP .