



## Full Length Article

# A novel surface imprinted polymer/magnetic hydroxyapatite nanocomposite for selective dibenzothiophene scavenging



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## ABSTRACT

Highly selective adsorbent for dibenzothiophene (DBT) was successfully designed and prepared. Molecularly imprinted polymer (MIP) and magnetic hydroxyapatite (MHAP) were used as building blocks for the novel nanocomposite adsorbent. MIP/MHAP was synthesized by grafting polymerization and surface molecular imprinting using DBT as a template molecule. The microstructure and morphology of the designed nanoadsorbent were examined via FTIR, SEM and VSM. Specific surface area and pore size distribution were determined by Quantachrome Nova 3200S automated gas sorption apparatus. Additionally, static adsorption experiments, isotherms and selective recognition adsorption studies were carried out. Reversed-phase high performance liquid chromatography (RP-HPLC) was used to determine DBT. The experimental data exhibits excellent adsorption capacity for DBT reaches 247 mg/g within 60 min. Competitive adsorption results proved that MIP/MHAP have a greater affinity towards DBT molecules than benzothiophene analogues. Pseudo-second-order model and the Langmuir isotherm were used to describe the adsorption process.

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## 1. Introduction

Combustion of high sulfur content fuel has serious environmental and health impacts [1,2]. Therefore, health organizations and governments have mandated restricted specifications for sulfur levels in fuel and exhausts [3,4]. In addition to eco-impacts, sulfur compounds in fuel cause poisoning of catalysts and electrodes in fuel cell system [3]. Dibenzothiophene (DBT) and its derivatives account for a significant value of the total organic sulfur in crude oils, Fig. 1. They account up to 70% of the total sulfur content of West Texas crude oil and up to 40% of the total sulfur content of Middle East crude oils. [5].

Many techniques for desulfurization of fuel have been proposed, including hydrodesulfurization [6,7], extraction [8], biodesulfurization [9], adsorption [10], and membrane desulfurization [11,12]. Most of those methods focused on process optimization and performance. However, desulfurization by molecular imprinting method is quite insufficient.

Molecular imprinting technique based on creating artificial recognition sites in polymeric matrices complementary to the template molecules in their shape, size and functional groups [13,14]. In this technique, functional monomer and cross-linker are copolymerized in presence of template molecule. When the template molecule is removed from the bulk of polymer matrix after copolymerization, it leaves imprinted recognition sites and cavities complementarily to the shape, size and functionality of the template [15,16] forming what is called molecularly imprinted polymer (MIP). Unfortunately, most previous studies show that the conventional bulk MIP has intrinsic limitations, such as low adsorption capacity, poor site accessibility and irregular shape [17]. To overcome these limitations, surface imprinting technique has been proposed [18]. In this modified technique, the recognition sites are formed at the surface of the polymeric material. Those new sites are more easily accessible with favorable binding kinetics. MIP prepared by surface imprinting technique has high affinity sites and cavities. This approach in designing imprinted polymer can not only avoid grinding and sieving steps but also obtains regular MIP composites with abundant sites and cavities on the surface.

Available literature shows that the maximum adsorption capacities recorded for removal of Dibenzothiophene by MIP technique were varied from 10 to 182 mg/g [19–30].

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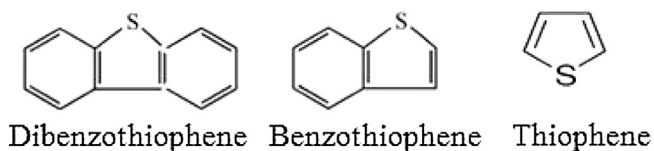


Fig. 1. Dibenzothiophene and its structural analogues.

The amazing solid-liquid separation of magnetic nanocomposites and their high adsorption capacities make them valuable candidates for in situ or ex situ removal of contaminate [31–33]. The aim of this study is to design molecularly imprinted polymer/magnetic hydroxyapatite nanocomposite as a novel selective adsorbent for dibenzothiophene removal.

## 2. Experimental

### 2.1. Materials

DBT (98%), benzothiophene (BT, 99%), thiophene (T, 99%), 4,6-DMDBT, ethylene glycol dimethacrylate (EGDMA) (98%), toluene, glacial acetic acid, methanol (MeOH), ethanol, *n*-octane and benzoyl peroxide,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , ammonium hydroxide (25%, w/v) were all purchased from the Sigma Chemical Company.

### 2.2. Preparation of hydroxyapatite (HAP)

The nano-sized hydroxyapatite was prepared by the wet chemical method. First, ammonium hydroxide (25%) was added carefully to 0.25 M phosphoric acid with stirring until we get a solution with pH=10. Next, 1 M calcium nitrate tetrahydrate solution was mixed slowly with the above phosphoric acid-ammonia solution and stirred vigorously for 1 h. The gel obtained after aging at room temperature for 24 h was dried at 80 °C for another 24 h in a dry oven. The produced (HAP) powder was washed by distilled water several times and sintered for 2 h at 600 °C.

### 2.3. Preparation of magnetic hydroxyapatite (MHAP)

HAP powder (2 g) was mixed ultrasonically with 80 mL of 1.25 M  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 2.5 M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  mixture. Then the mixture was purged with nitrogen gas and stirred vigorously at 80 °C. 10 mL of ammonium hydroxide (25%, w/v) was added drop by drop, and the reaction was maintained for 30 min. The black product of MHAP was collected by a magnet and washed several times by distilled water and dried in a vacuum oven at 50 °C for 24 h.

### 2.4. Preparation of MIP/MHAP

A typical procedure for preparing MIP/MHAP is as following: 0.368 g DBT and 0.2083 styrene were dissolved in 10 mL of toluene with 2 g of dispersed MHAP and stirred for 4 h. Then 7.9 g EGDMA and 0.122 g benzoyl peroxide were added to the solution under nitrogen atmosphere. After hyper acoustic mixing, the mixture was then polymerized overnight by thermal initiation at 60 °C. The resultant polymer was coded as (MIP/MHAP+DBT). The freed DBT in the formed polymer was continuously extracted and washed with methanol/acetic acid solution (9:1, v/v) until no sulfur was detected by the Sulfur Analysis Instrument. DBT free MIP/MHAP was washed by ethanol, dried overnight and kept for further investigation. For comparison purposes, surface nonimprinted polymers (NIP/MHAP) were also prepared in the same way in absent of DBT template molecules. Preparation scheme is illustrated in Fig. 2.

### 2.5. Characterization of the prepared samples

Function groups and bonds were identified by FTIR spectrometer Perkin Elmer (model spectrum one FT-IR spectrometer, USA). Samples were prepared using the standard KBr pellets and spectra were recorded between 4000 and 400  $\text{cm}^{-1}$ . Morphology of prepared samples was imaged using transmission electron microscope (Tecni G20, FEI, Netherland) and a scanning electron microscope (Quanta 250 FEG, FEI, Netherland) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K. V magnification 14 x up to 1,000,000 and resolution for Gun.1n). Specific surface area was measured from the  $\text{N}_2$  adsorption-desorption isotherms at liquid nitrogen temperature (−196 °C) using Quantachrome Nova 3200 S automates gas sorption apparatus. Prior to such measurements all samples were perfectly degassed at 300 °C for six hours and under vacuum pressure  $1.3 \times 10^{-3}$  Pa. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM, 735VSM, Model 7410; Lake Shore, Westerville, Ohio, USA) with a maximum magnetic field of 31 kOe.

### 2.6. Adsorption experiments

DBT/*n*-octane stock solution of (1000 mg/L) was prepared as a source of DBT; *n*-octane was used as feed model oil. The running solutions were diluted from the stock based on the need. All adsorption experiments were performed in batch mode. In a model one, MIP/MHAP or NIP/MHAP (1.2–60 mg) was added to 10 mL DBT/*n*-octane (150–1000 mg/L) in 20 mL flasks and shaken for (30–120 min) at temperature of (303–343 K) and constant speed of 200 rpm. Reversed-phase high performance liquid chromatography (RP-HPLC) was used to determine DBT in the filtrate. The separation was performed on C18 column (250 × 4.6 mm, 5  $\mu\text{m}$ ), with the mobile phase of Acetonitrile- $\text{H}_2\text{O}$  (45:55, v/v). The flow rate was 0.8 mL/min and the detection wavelength was 230 nm.

The equilibrium adsorption capacity was calculated according to the following equation [34,35].

$$\text{Theadsorptioncapacity}(\text{mg/g}) = (\text{C}_0 - \text{C}_e)V/m \quad (1)$$

Where  $\text{C}_0$  and  $\text{C}_e$  are the initial and equilibrium concentrations of DBT (mg/L), respectively,  $V$  is the volume of solution (L) and  $m$  is the mass of adsorbent (g). All tests were set in triplicate and average values were given.

## 3. Results and discussion

### 3.1. Polymer characterization

#### 3.1.1. Infrared spectrum analysis

FTIR spectra of MHAP, MIP/HAP, NIP/MHAP and MIP/MHAP+DBT are demonstrated in Fig. 3. Stretching peaks at 1140 and 1730  $\text{cm}^{-1}$  corresponds to C–O and C=O in EGDMA, respectively. Absorption intensity of C=O peak weakened obviously in MIP/MHAP+DBT spectrum which could be attributed to steric hindrance effect that restrain full vibration of carbonyl group. The original cross-linking agent EGDMA and styrene have abundant vinyl groups. However, the characteristic C=C peaks at 1630, 990, and 910  $\text{cm}^{-1}$  show low intensity that verified the crosslinking polymerization reaction. After surface grafting, a new vibrational peak appears in the three polymer samples around 2990–2995  $\text{cm}^{-1}$  belongs to aliphatic C–H stretching vibration. Additionally, flexions at 700–1000  $\text{cm}^{-1}$  corresponding to aromatic C–H bond can be seen in the spectra. Peaks observed at 1313, 1185 and 1046  $\text{cm}^{-1}$  related to the =C–H in-plane vibration and the =C–H out-of-plane vibration is found at 617 and 918  $\text{cm}^{-1}$ .

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