Full Length Article

Thermodinamic study of a magnetic molecular imprinted polymer for removal of nitrogenous pollutant from gasoline

Liz Nayibe Martínez Saavedra[a], Bruno Eduardo Lobo Baeta[a], Márcio César Pereira[b], Luiz Carlos Alves de Oliveira[c], Adilson Candido da Silva[a,*]

[a] Departamento de Química, Instituto de Ciências Exatas e Biológicas (ICEB), Universidade Federal de Ouro Preto (UFOP), 35400-000 Ouro Preto, Minas Gerais, Brazil
[b] Instituto de Ciência, Engenharia e Tecnologia (ICET), Universidade Federal dos Vales do Jequitinhonha e Mucuri (UFVJM), Campus Mucuri, 39803-371 Teófilo Otoni, Minas Gerais, Brazil
[c] Departamento de Química, Universidade Federal de Minas Gerais (UFMG), 31270-901 Belo Horizonte, Minas Gerais, Brazil

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ABSTRACT

In this work, magnetic molecularly imprinted polymers (MMIP) and magnetic non-imprinted polymers (MNIP) were tested as selective adsorbents for quinoline in n-heptane. The synthesis was carried out using chloroform as a porogenic solvent and maghemite (γ-Fe2O3) as the magnetic component. The thermogravimetric data revealed that the MMIP and MNIP are formed by 73 and 81 wt% of the polymer, respectively. The powder X-ray diffraction patterns of the MMIP and MNIP confirmed that the magnetic component in the polymers was maghemite. The adsorption equilibrium data of quinoline displayed that the Sips models better fitted the isotherms. The maximum quinoline adsorption capacity (q_{max}) at 298 K was 25 and 14 mg g^{-1} for the MMIP and MNIP, respectively. The kinetics of quinoline adsorption followed the Elovich model. The negative values observed for the Gibbs free energy ($\Delta G°$) suggest a spontaneous adsorption while the enthalpy values ($\Delta H°$) indicate that the quinoline was attached to the polymers by physisorption. Selectivity tests showed that the MMIP was about 6 times more selective than MNIP for quinoline adsorption. Also, the MMIP was efficient to remove quinoline from a complex matrix of gasoline (10.35 mg/g). Because of its magnetic properties, the MMIP could be easily recovered and reused for at least five adsorption cycles without significant loss in the adsorption capacity.

1. Introduction

Concerns at a global level with the increased contamination rate of the air, water, and soil caused by the industrial developments have imposed stricter control measures against the emission of pollutants. Heterocyclic nitrogen and sulfur compounds have received particular attention in the last years regarding the generation of toxic molecules such as NO_x and SO_x during their combustion [1]. Therefore, the removal of these compounds from complex matrixes such as those found in fuels is a significant challenge.

In the last years, the stricter environmental standard has been imposed with the aim of decrease the level of these contaminants in the oil. In Brazil, the level of sulfur present in the diesel was reduced to less than 50 ppm while for countries of European Union it must be than 15 ppm [2–5].

Nowadays, the most used processes for the removal of heterocyclic nitrogen and sulfur compounds are based on hydrotreatments as hydrodenitrification (HDN) and hydrodesulfurization (HDS), which are

well-known catalytic processes in the refining industries. However, the nitrogen compounds as the quinoline in the oil may hamper the efficiency of such process, since these compounds are known to cause the poisoning of the catalyst. Thus, technologies such as HDN and HDS used for the removal of benzothiophene (BTs), dibenzothiophene (DBTs) and indoles have not been efficient [6]. It should be emphasized that only a small concentration equivalent to 5 ppm of quinoline is enough for poisoning the catalyst [2].

An alternative for increasing the efficiency of the hydrotreatments consists of removing the sulfur and nitrogen compounds by adsorption on the surface of nanomaterials. However, the use of universal adsorbents as activated carbon has some drawbacks such as low reuse capacity and low selectivity. To solve these drawbacks the design of selective adsorbents based on molecularly imprinted polymers (MIP) has been proposed [7,8].

The MIPs are prepared by the bulk copolymerization of functional monomer and cross-linker in the presence of a template molecule. After polymerization, the material needs to be mechanically crushed, which

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* Corresponding author.
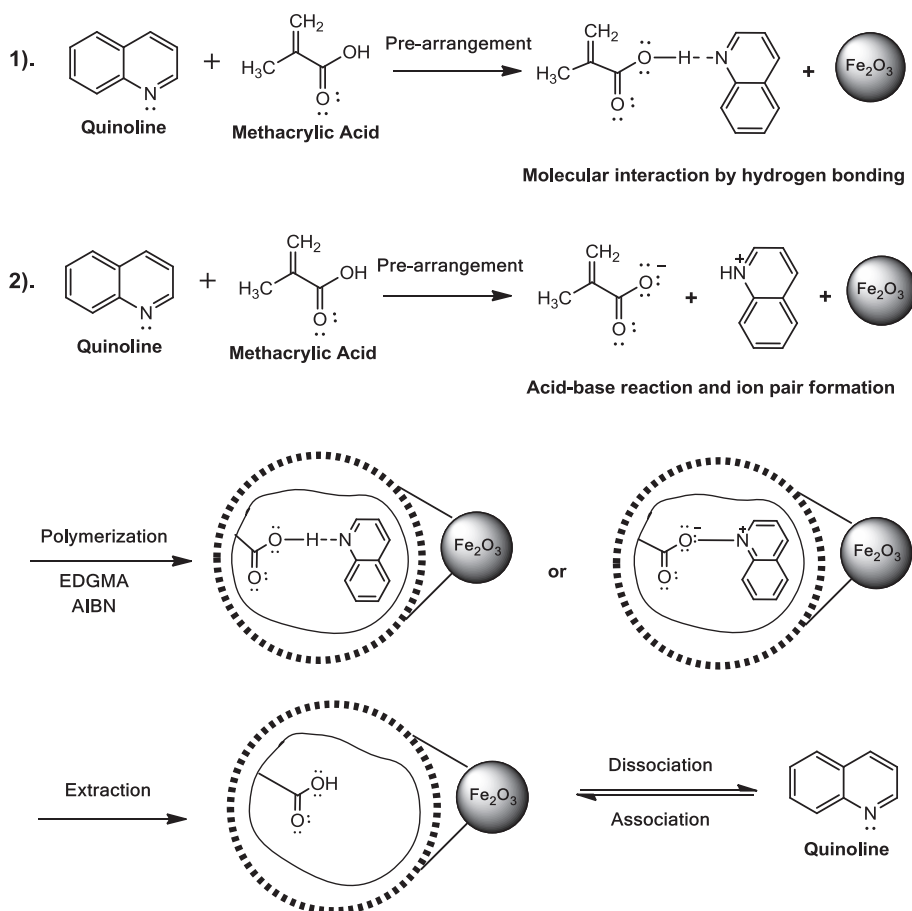 E-mail address: adilsonufla@gmail.com (A.C. da Silva).

Fig. 1. Schematic process for the MMIP preparation.

results in particles with an irregular shape. Irregular particle size may hamper its use in adsorption column. Alternatively, the MIPs synthesized by the bulk method can be utilized in a continuous stirred–tank reactor. However, by this process, the recovery of the MIP adsorbent from the fluid is difficult to perform. Therefore, in this paper, we focus on the synthesis of a magnetic molecularly imprinted polymer (MMIP). The magnetic properties of these materials allow them to be easily recovered in magnetic separators [9–11]. After separation, the template can be extracted and the MMIP adsorbents reused.

Extensive efforts have been made to synthesize and utilize these materials as selective adsorbents. The few studies reported on the use of MMIP adsorbents for removing pollutants derived from petroleum [8,17], dyes [18], and antibiotics [19,20] have shown to be efficient. Therefore, in this work, it was developed magnetic molecularly imprinted polymers (MMIP) to be used as selective adsorbents for quinoline contaminated liquids. The kinetic and thermodynamic studies on quinoline adsorption by MMIP in n-heptane and gasoline were described in detail.

2. Materials and methods

2.1. Chemicals

Quinoline (98%), Dibenzothiophene (98%), Carbazole (≥95%), methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), and 2, 2′-azobisisobutyronitrile (AIBN) were purchased from Sigma Chemical Company, U.S.A. Toluene (Quimex), cyclohexane (Dinâmica), methanol, NaOH (Synth), and n-Heptane (Neon Ltda) were acquired from Brazilian Chemical Industries. Glacial acetic acid (Merck KGaA) from Germany. All chemicals were used as received from the manufacturer without additional purification.

2.2. Apparatus

Thermogravimetric analyses were performed on an SDT2960 from room temperature to 1000 °C with a rate of 10 °C per minute under an inert atmosphere of N_2. FTIR spectra were scanned in a range of 400–4000 cm^{-1} using an ABB Bomem FTIR spectrometer equipped with accessories of diffuse attenuated reflectance (DRIFT). The quantification and identification of quinoline, dibenzothiophene, and carbazole were carried out on a spectrophotometer UV–VIS (Hewlett Packard 8453) in the wavelength of 314 nm, and on a Gas Chromatograph BID 2010 Plus SHIMADZU equipped with plasma detector and a column SH-Rtx-5. SEM images were carried out on a JSM-5500 scanning electron microscope. Surface area and porosity were determined from adsorption experiments using an AutosorbIQ surface area and pore size analyzer. X-ray diffraction analyses were performed using a Panalytical Empyrean diffractometer equipped with a graphite monochromator, nickel filter and CuKα radiation (λ = 1.54056 Å, 40 kV, and 20 mA). For the analysis of the polymers, a scanning (2θ) of 10–80° and step of 0.5° min^{-1} was applied.

2.3. Preparation of γ-Fe₂O₃

γ-Fe_2O_3 nanoparticles were prepared by dissolving 5.56 g Fe $(SO_4)_2(NH_4)_2·6H_2O$ in highly purified water. After this stage 100 mL of NaOH (2 mol L^{-1}) were added slowly drop by drop until the formation of a green precipitate. After the formation of a precipitate, 5 mL of H_2O_2 30% (v/v) were immediately added with continuous stirring. The precipitate was washed several times with distilled water and dried in a vacuum desiccator at room temperature.