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Ionic liquid functionalized nanoporous silica for removal of anionic dye

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ABSTRACT

Nanoporous silica (NPS), with an average pore diameter of 2.4 nm and a surface area of 949 $m^2\ g^{-1}$, was synthesized by using nonyl phenol ethoxylated decylether (NP-10) and ethyl silicate 40% (ETS-40) under acidic condition. Ionic liquid functionalized adsorbent was prepared by grafting of N-methyl-N′-propyltrimethoxysilylimidazolium chloride onto NPS for removal of methyl orange. The adsorbent was characterized by means of small-angle X-ray scattering, scanning electron microscopy, N_2 adsorption–desorption isotherms, thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) and Raman spectroscopy. The kinetic data revealed that the adsorption process is consistent with the pseudo-second-order model. The Langmuir isotherm showed better correlation with the experimental data. The monolayer adsorption capacity of adsorbent was found to be 135 mg g^{-1}. Thermodynamic parameters such as enthalpy change ($\Delta H^\circ = +61.72$ kJ mol^{-1}), free energy change ($\Delta G^\circ < 0$) and entropy change ($\Delta S^\circ = +222$ J mol^{-1} K^{-1}) indicate the endothermic and the spontaneous nature of the adsorption.

1. Introduction

NPS materials have attracted more attentions due to their interesting and wide applications in the field of catalysis, drug delivery, adsorption and separation [1–8]. Since the discovery of M41S, different kinds of nanoporous silicas have been synthesized by using various surfactants as structure directing agents (SDAs). Nonionic surfactants, especially polyethylene oxide, are extensively used as SDAs due to their low-cost, biodegradable and non-toxic characteristics [9]. The family of MSU-X (X = 1-4) silica was prepared under neutral conditions by hydrogen bonding interaction where X refers to the nonionic surfactant molecules that can be either alkyl PEO, alkyl–aryl PEO, polypropylene oxide PEO block copolymers or ethoxylated derivatives of sorbitan fatty esters, respectively [9,10]. MSU-X compounds have a wormhole-like pore structure which facilitates the diffusion of reacting species to the reactive site [11]. It should be noted that the common source of silica used in the synthesis of NPS is alkyl orthosilicates such as TEOS and TMOS. Their high cost and low content of SiO_2 (28%) make them impracticable for commercial scale-up. ETS-40 is commercially available and can be used as an economical source. The synthesis of NPS using this silica source was rarely reported [12]. The surface functionalization of NPS has altered the interfacial chemistry. There are more and more research interests on ionic liquid-modified NPS recently because of environmentally friendly media of ionic liquid and extensive applications in the catalysis, enzyme immobilization and adsorption [13–17].

The rapid growth of industries produces large amounts of pollutants. Synthetic dyes are an important water contaminant which they have been widely used in textile, leather, cosmetics, plastics, and food industries [18]. These colored effluents not only have a negative effect on the aquatic system because of blocking sunlight for photosynthesis process but also can be identified as the toxic and carcinogenic materials [19]. Azo dyes are the most common group of dyes used in textile industries because of their low cost, stability and variety of colors [20]. NPS modified with different functional groups such as amino, carboxylic and polyelectrolyte has been used for the removal of dyes from wastewater [21–23].

In this study, the simple, cost-effective and short-time synthesis route of NPS by using NP-10 as a SDA and ETS-40 as a silica source in acidic media was introduced. According to the literature, there is little consideration regarding the removal of synthetic dyes utilizing ionic liquid functionalized NPS. The adsorbent was prepared using ethanol as an eco-friendly solvent for the removal of methyl orange as an azo dye. The adsorption behavior was evaluated by kinetic and thermodynamic studies.

2. Experimental

2.1. Materials

The chemicals used for the synthesis: ethyl silicate solution (ETS-40, Wacker, SiO_2 40%), nitric acid (Merck, 65%), nonyl phenol ethoxylated decylether (Hulls, NP-10, Mw = 660 g mol^{-1}), N-methyl imidazole (Merck, $M_w = 82.11$ g mol^{-1}), 3-chloropropyltrimethoxy silane (Merck, $M_w = 198.72$ g mol^{-1}), methyl orange (Aldrich, Mw = 327.34 g mol^{-1},

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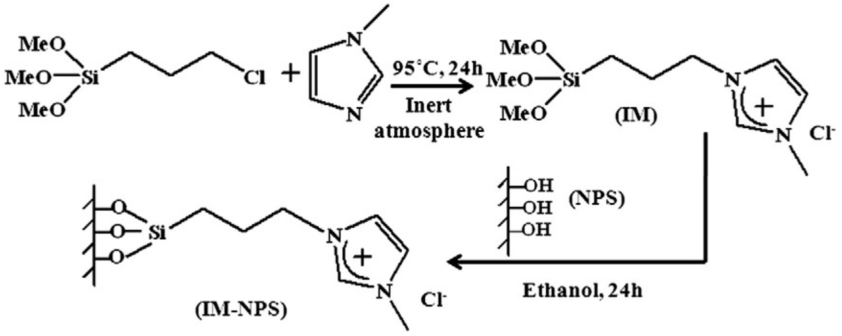

Fig. 1. Synthetic route of IM-NPS.

hereafter designated as MO), ethanol and dionized water. All commercial chemicals were employed without any purification.

2.2. Synthesis of nanoporous silica (NPS)

NPS was prepared using NP-10 as a SDA and ETS-40 as a silica source under acidic conditions. Briefly, 50 g of NP-10 was dissolved in a solution containing 334 ml HNO_3 and 2.6 L H_2O under stirring at 30 °C. Then, 196 g ETS-40 was added to this solution and it was kept at 80 °C under stirring at 400 rpm during 5 h. The solid product was filtered, washed with deionized water and dried. The final compound was recovered after ethanol extraction with a Soxhlet apparatus and a further calcination at 600 °C for 6 h in air in order to complete removal of the surfactant molecules.

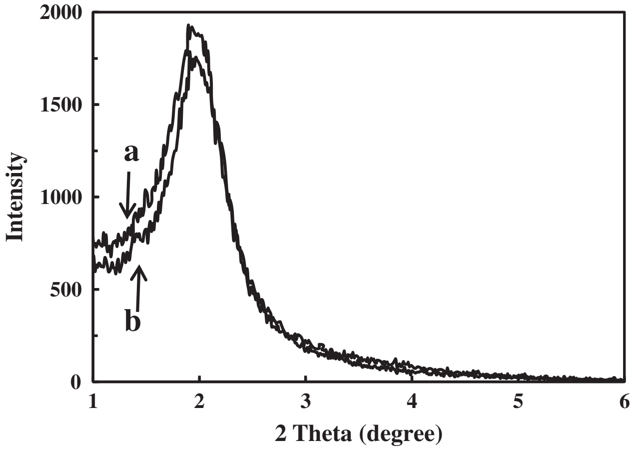

Fig. 2. SAXS pattern of (a) NPS after calcination and (b) IM-NPS.

2.3. Functionalization of NPS

2.3.1. Synthesis of the N-methyl-N′ propyltrimethoxysilylimidazolium chloride (IM)

IM was prepared according to Valkenberg's report [24]. Typically, a mixture of N-methylimidazole (56.7 g, 0.690 mol) and 3-(chloropropyl) trimethoxysilane (137.17 g, 0.690 mol) were stirred in a dry 100 ml flask under nitrogen flow at 95 °C for 24 h. After cooling at room temperature, the resulting liquid product was extracted with ether. The final material obtained was a yellow viscid liquid.

2.3.2. IM-functionalized of NPS (IM-NPS)

The synthetic route of IM-NPS is summarized in Fig. 1. In a typical synthesis, 1 g of NPS was dried and added to the solution of 6 mmol of IM and 20 ml of ethanol and stirred for 24 h at room temperature. The product was filtered and washed repeatedly with ethanol to remove the unreacted materials. Finally, it was dried in the oven at 100 °C for 2 h.

Table 1
Textural characteristic of NPS and IM-NPS.

Sample	$S_{BET}(m^2\ g^{-1})$	$V(cm^3\ g^{-1})$	D (nm)[a]
NPS	949	0.48	2.4
IM-NPS	290	0.15	2.4

[a] Pore diameter calculated by BJH method.

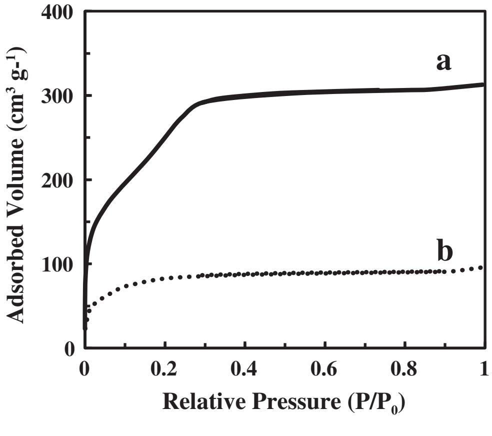

Fig. 3. N_2 adsorption–desorption isotherms of (a) NPS and (b) IM-NPS.

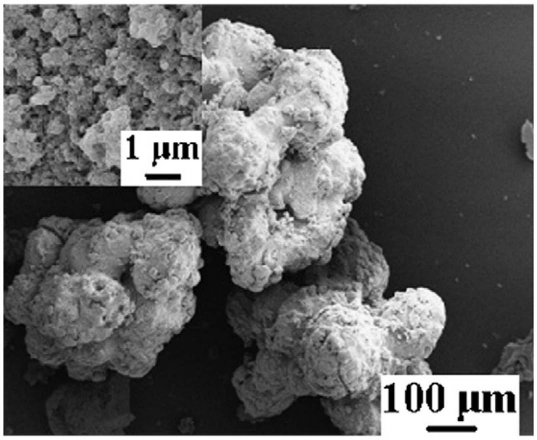

Fig. 4. SEM image of NPS.