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Adsorption of Remazol Red 3BS from aqueous solutions using APTES- and cyclodextrin-modified HMS-type mesoporous silicas

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ABSTRACT

The removal of Remazol Red 3BS (C.I. 239) dye by HMS ordered mesoporous silica, aminopropyl-modified HMS (HMS-NH_2) and β-cyclodextrin-modified HMS (HMS-CD) materials was studied in the present work. The modified materials were functionalized in situ by adding the organic modifiers (3-aminopropyltriethoxysilane and a silylated derivative of MCT-β-CD) in the synthesis mixture and using dodecylamine as the mesopore structure directing agent. The successful incorporation of aminopropyl groups in HMS-NH_2 and of cyclodextrin moieties in HMS-CD was verified by means of FT-IR spectroscopy, elemental analysis and N_2 porosimetry. The HMS-CD material exhibited significantly higher adsorption capacity compared to that of the HMS-NH_2 material, while the parent HMS mesoporous silica showed negligible adsorption capability. The maximum adsorption capacities obtained (at the optimum pH 2) on the basis of the Langmuir analysis were 0.28 mmol/g for HMS-CD and 0.14 mmol/g for HMS-NH_2. It was shown that the HMS-CD sorbent can be effectively regenerated by the surfactant-enhanced regeneration method using SDS and that can be reused without significant loss of its adsorption capabilities.

1. Introduction

Over the last few decades, adsorption has been recognized as an efficient separation process and has become an attractive option for the removal of azo-dyes from industrial effluents. Activated carbons are among the most effective adsorbents because of their excellent adsorption capacity for organic targets [1,2]. However, their use is sometimes problematic mainly due to their relatively high cost and regeneration problems [3]. When carbon beds become saturated, the carbon must be regenerated before the bed can be reused. Regeneration of activated carbon is a major factor in the cost effectiveness of the use of carbon. The standard method of regeneration (thermal regeneration) involves removal of the carbon from the bed, transport to a regeneration furnace where the adsorbed organics are volatilized and carbonized and loading the bed with the regenerated carbon. This process is energy intensive, labour intensive and time consuming. Further, up to 30% of the carbon may be burned in the furnace [4]. Additionally, the microporous nature of the majority of activated carbons limits their use as molecular sieves of small molecules than of bigger ones as azo-dye molecules. For the latter, sorbents with larger pores preferably in the mesoporous range would be employed [5–9].

Ordered mesoporous silicas represent a class of materials that can be used as adsorbents [10]. The most important characteristics of the mesoporous silicas are the large surface area, high mesopore volume, and narrow pore size distribution in the range of mesopores. However, many applications (such as adsorption, ion exchange, catalysis and sensing) require these silica-based materials to have specific attributes such as binding sites, stereochemical configuration, charge density and acidity [11]. Functionalization of the silica surface with organic groups is very important and can be achieved via postsynthesis grafting or direct co-condensation synthesis routes [12,13].

Cyclodextrins (abbreviated herein as CDs) are glucose-based molecules produced from the enzymatic degradation of starch by bacteria. They are cyclic oligosaccharides consisting of 6 (α), 7 (β), or 8 (γ) glycopyranose units, which are joined together by α(1–4) linkage forming a torus-shaped ring structure. The exterior sides of them are hydrophilic for the outward hydroxyl groups, while the interior cavities are hydrophobic, so they can behave as hosts for various molecules. The most characteristic feature of CDs is the ability to form inclusion complexes with organic molecules, including dyes, through host–guest interactions [14,15]. Organic pollutants can thus be trapped in the hydrophobic cavity of CDs. Using cyclodextrins, highly toxic substances can be removed from industrial effluent by inclusion complex formation. CDs themselves however are highly water-soluble and must therefore be grafted onto a stationery phase, such as polymers or porous silicas [16–19].

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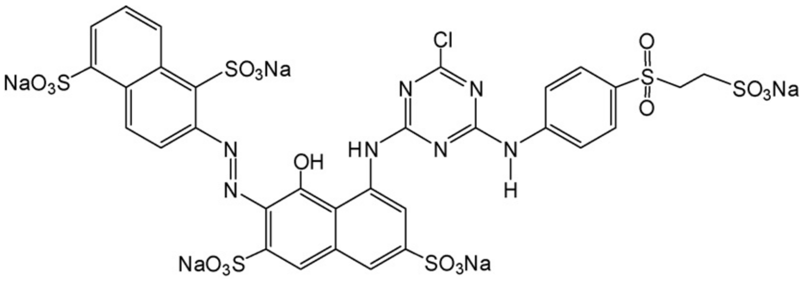

Fig. 1. Chemical formula of Remazol Red 3BS (C.I. 239).

The removal of Remazol Red 3BS, which is often used in the textile industry, from aqueous solutions has been already studied by (i) sorption onto micro/mesoporous carbons, (ii) retention by nanofiltration membranes, (iii) degradation by catalase peroxidase/commercial laccase and (iv) flotation [6,20–24]. In the present work we report the adsorption of Remazol Brillant Red 3BS by using HMS ordered mesoporous silica. HMS has been successfully modified with cyclodextrin in a one-step synthesis via co-condensation reaction of tetraethoxysilane and a silylated derivative of monochlorotriazinyl β-CD, according to previously reported methods [16]. The adsorption capacity and kinetics were studied using the batch method. The performance of the cyclodextrin functionalized material was compared to that of 3-aminopropyltriethoxysilane (APTES)-functionalized HMS silica, also prepared via one-pot synthesis method. Desorption of the dye and regeneration ability of the mesoporous silica sorbents were also investigated.

2. Experimental

2.1. Materials

The reactive dye used as adsorbate was the Remazol Red 3BS (C.I. 239, purity 99%) with molecular weight of 1085.84 (g/mol) and was obtained from DyStar. The molecular structure of the dye is shown in Fig. 1. The number of ionizable groups in the dye molecule were 5, while the number of polar functional groups were 21 (S–O:17; C–O:1; –Cl:1; –NH:2). The molecular size (mean kinetic diameter) of the dye was estimated to be 1.2 nm using the WINMOPAC program. All chemicals used in synthesis and adsorption experiments were purchased from Sigma–Aldrich Ltd. (except for the monochlorotriazinyl β-cyclodextrin (MCT-β-CD) that was supplied by Wacker Biochemie Chemical Company) and were used without further purification. The structure of MCT-β-CD consists of β-cyclodextrin to which electrophilic chlorotriazinyl groups (MCT, $-OC_3N_3ClO^-Na^+$) have been attached (with an average of 2.80 MCT groups per β-CD molecule). The chemical formula of MCT-β-CD can therefore be expressed as $C_{42}O_{35}H_{53.2}(ClC_3N_3O^-Na^+)_{2.8}$ [16]. Doubly distilled water was used in all experiments.

2.2. Synthesis of mesoporous HMS, HMS-NH_2 and HMS-CD silica sorbents

The HMS mesoporous silica was synthesized following the method that leads to the formation of wormhole-like structure with high textural (interparticle) porosity [25]. In a typical synthesis, dodecylamine (DDA) which is used as mesostructure directing agent (template), was dissolved in ethanol followed by addition of water (water/ethanol = 90:10, v/v). Tetraethylorthosilicate (TEOS) used as silica source was then added slowly and the mixture was stirred for 18 h at room temperature. The white product was filtered, washed with water and dried at room temperature for 24 h and at 90 °C for 3 h. The reaction mole stoichiometry was 1 TEOS:0.25 DDA:4.38 EtOH:127.50 H_2O. Efficient extraction of the template (dodecylamine) from the formed mesostructure was achieved by refluxing the solid with 0.10 M aqueous solution of HCl for 2 h, so that the amine groups were transformed into easily solubilized ammonium groups associated with chloride ion ($-NH_3^+$, Cl^-) [26].

An APTES-modified HMS mesoporous sample (denoted HMS-NH_2, see Fig. 2) was synthesized by the direct synthesis route which involves co-condensation of TEOS and APTES using dodecylamine as the structure directing agent and a reaction stoichiometry of 0.90 TEOS:0.10 APTES:0.27 DDA:7.90 EtOH:29.40 H_2O [27]. To a stirred solution of dodecylamine in ethanol/water mixture (10:90, v/v) was added separately but simultaneously and rapidly, TEOS and APTES. A white precipitate was observed after few minutes of reaction. The

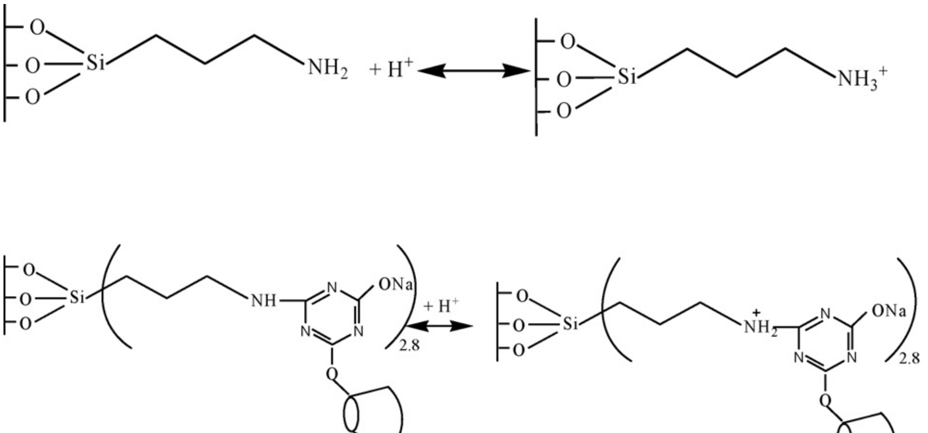

Fig. 2. HMS modification (a) HMS-NH_2 and (b) HMS-CD.