



Direct synthesis of pore-expanded amino-functionalized mesoporous silicas with dimethyldecylamine and the effect of expander dosage on their characterization and decolorization of sulphonated azo dyes

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ABSTRACT

With harmless reagents, a series of pore-expanded amino-functionalized mesoporous silicas (PEAFMS) were directly synthesized under mild alkali condition. During the preparation, dimethyldecylamine (DMDA) served as the expander. The PEAFMS samples (S_0 , $S_{0.50}$, $S_{1.00}$, $S_{1.50}$ and $S_{2.00}$), which were prepared using different DMDA/surfactant (cetyltrimethylammonium, abbr. CTAB) molar ratio of 0, 0.50, 1.00, 1.50 and 2.00, were characterized by FTIR spectroscopy, CHN elemental analysis, X-ray diffraction and N_2 adsorption measurement. Results demonstrated that the addition of DMDA markedly influenced the porous structures of synthesized samples. Their pore sizes and pore volumes were adjusted in the range from 4.684 to 22.31 nm and from 0.6046 to 1.360 cm^3/g , respectively. Subsequently, the adsorption mechanism of sulphonated azo dyes onto obtained PEAFMS samples was analyzed and the optimal pH was determined as pH 2. The synthesized decolorants were then compared for the removal of given dyes (acid mordant dark yellow GG and reactive red violet X-2R) from aqueous solutions and the degressive order of adsorption capacities for two dyes was $S_{1.50} > S_{2.00} > S_{1.00} > S_{0.50} > S_0$. The experimental results confirmed that the use of DMDA could improve the decolorization performance of functionalized mesoporous silicas. The sample synthesized with DMDA/CTAB molar ratio of 1.50 owned the suitable pore size (19.04 nm) and pore volume (1.360 cm^3/g), so it exhibited better decolorization ability than counterparts. The adsorbed amount of acid mordant dark yellow GG and reactive red violet X-2R reached 1.713 and 0.902 mmol/g, respectively.

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1. Introduction

The effluents of sulphonated azo dyes (the most numerous of synthetic azo dyes) [1] are extensively derived from textile, leather and many other industries. Due to their good water solubility and potential mutagenicity/carcinogenicity of their degradation products [2,3], dyes are causing serious environmental pollution and threatening people's health, even at low concentrations. Thus dye removal is yet one of challenging tasks for ecological protection.

Among the numerous techniques of dye removal, adsorption has proven as an attractive and effective method in terms of flexibility, water reuse and waste recovery, simplicity of design, ease of operation and insensitivity to toxic pollutants. Activated carbon is the most popular adsorbent [4,5], but certain factors such as high cost and regeneration trouble limit its widespread applications. More importantly, the adsorption performance of commonly used activated carbon depends on various characteristics such as surface

area, pore structure and pore size distribution; however, the pores of activated carbon are principally distributed in the micropore (pore size <2 nm) region. So large molecules such as dyes cannot easily penetrate into the micropores and efficiently adsorb on them. As a consequence, activated carbon shows the unsatisfactory adsorption capacity for dyes [6–8]. In recent years, alternative adsorbents have been investigated, such as castor seed shell [9], rice straw [10], sawdust [11], perlite [12], durian peel [13], coconut-husk [14], kaolinite clay [15], chitosan [16] and soybean hull [17] etc. Most of these alternative adsorbents, though easily available and low-cost, present some deficiencies: poor mechanical and heat resistance, relatively high loss ratio and limited adsorption capacity for dyes. So researchers are still impelled to focus on novel adsorbents.

Mesoporous silicas, with good stability, large surface area and tunable pore size in the range of 2–50 nm, are attracting increased attention since being synthesized in 1992 [18]. Owing to their uniform mesopores and flexible modification with various functional groups, these materials have many potential applications in the fields of adsorption, catalysis and separation. Recently, different

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kinds of functionalized mesoporous silicas have been reported to be effective adsorbents for environmental pollutants such as dyes [19–22] and the decolorization efficiency of mesoporous silicas is highly dependent on the pore size. Pore-expanded mesoporous silicas with functional groups have been confirmed to possess excellent adsorption performance for bulky dye molecules [23,24]. As a result of larger pore channels and better pore connectivity, specific functional groups modified on the silica surface can interact with various adsorbates more efficiently (e.g. amino groups show remarkable adsorption properties for sulphonated azo dyes [23]).

At present, three conventional methods have been used for pore expansion of mesoporous materials: (1) increasing the chain length of surfactants ($n \leq 16$) [18] or using copolymer as templates [25]; (2) post-synthesis hydrothermal treatment [26]; (3) the use of expanders (e.g. alkanes [27], amines [28] and trimethylbenzene [29]). All of the information obtained showed that pore expansion easily led to a decrease of ordered mesostructure. Therefore, most researchers cautiously chose pore-expanded method and enlarged pore size slightly to maintain the long-range ordering of the mesostructure. In fact, long-range ordering of mesopores and very narrow pore-size distributions (PSDs) are not necessary for their application in the fields of environmental protection [30]; hence, the preparation and application of disordered mesoporous silicas with expanded pores have gradually received considerable attention [28]. Accordingly, Sayari et al. [31] reported that in the presence of dimethyldecylamine (DMDA), extra-large mesoporous silicas without modified groups were obtained using either direct synthesis or post-synthesis treatment. The presented experimental data showed that the addition of large amounts of DMDA, favored formation of the disordered mesostructure with remarkably high pore volumes (up to $3.3 \text{ cm}^3/\text{g}$) and large pore sizes (from 3.5 to 13.5 nm). The study also demonstrated that DMDA was undoubtedly a powerful expander and characteristics of the resulting mesostructure were closely related to the expander dosage.

Recent efforts have been focused on two-step synthesis of pore-expanded mesoporous silicas containing organic functional groups [23,29], and the two processes (pore expansion and modification of organic groups) are accomplished individually; however, little work has been carried out on direct synthesis of such mesoporous silicas. In comparison, direct synthesis is more convenient for the incorporation of “pore expansion” and “functionalization” processes in “one-step” procedure. In addition, common solvents and expanders used in synthesis of mesoporous silicas, such as mesitylene [29] and xylene [32], have high toxicity and are harmful to the environment. It is necessary to reduce the toxicity of solvents and expanders even choose harmless ones in view of green chemistry.

In this study, harmless reagents were selected and the direct synthesis of pore-expanded amino-functionalized mesoporous sil-

icas (PEAFMS) was attempted under mild alkali condition for decolorization of sulphonated azo dyes. A series of mesoporous silicas synthesized with different amount of DMDA (as expander) were prepared and characterized. Their decolorization behavior was subsequently investigated using acid mordant dark yellow GG and reactive red violet X-2R as model dyes. The adsorption capacity and mechanism of model dyes on the as-synthesized mesoporous silicas were also discussed.

2. Experimental

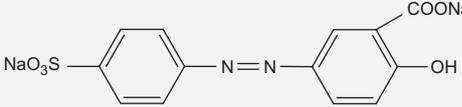
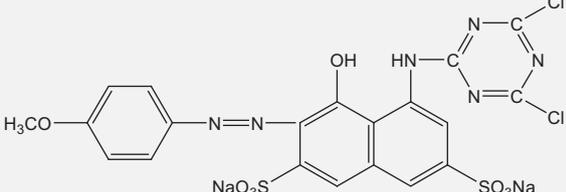
2.1. Reagents and materials

3-Aminopropyltriethoxysilane (APTES, 99%) and dimethyldecylamine (DMDA, 97%) were purchased from Aldrich. Tetraethyl orthosilicate (TEOS), cetyltrimethylammonium (CTAB), absolute ethyl alcohol, NaHCO_3 , HCl and NaOH were purchased from Shanghai Chemical Co. and tetramethylammonium hydroxide (TMAOH, w.t. 25%) was provided by Zhenfeng Chemical Co. Two sulphonated azo dyes, acid mordant dark yellow GG (Yellow) and reactive red violet X-2R (Red violet), were of commercial grade and obtained from Taopu Dyestuff Co. in Shanghai; their chemical structures, molecular weights and wavelengths corresponding to the maximum absorbance (λ_{max}) are shown in Table 1. All the above materials were used without further purification. Deionized water was used throughout this work.

2.2. Direct synthesis of PEAfMS

The direct synthesis of PEAfMS with DMDA as expander was carried out at room temperature, using APTES, TEOS, TMAOH, CTAB, ethanol and DMDA in relative molar ratios of 1.333:5.333:1.667:1:217.4:x; x is the molar ratio of DMDA to CTAB. It was 0, 0.50, 1.00, 1.50 and 2.00; and therefore resulted PEAfMS samples were marked as S_0 , $S_{0.50}$, $S_{1.00}$, $S_{1.50}$ and $S_{2.00}$, respectively. CTAB (2.19 g) was dissolved in 40 g of dry ethanol; then, different amount of DMDA was slowly added under vigorous stirring. Meanwhile, 1.76 g of APTES was stirred with 20 g of dry ethanol; subsequently, 3.6 g of 25% TMAOH aqueous solution was dropwise added. Two hours later, the above two solutions were mixed, followed by dropwise adding of TEOS (6.64 g). Then the mixture was slowly stirred for further 1 h. After reaction, the product was transferred into a petri dish for solvent evaporation at room temperature. The resulting solid was aged in deionized water at 368 K for 2 days. After recovered by filtration, the solid product was refluxed in ethanol/HCl for 1 day at 343 K to extract the surfactant templates. Then it was filtered, stirred in 1 mol/L NaHCO_3

Table 1
Chemical structures, molecular weights and λ_{max} of two sulphonated azo dyes.

Dye	Chemical structure	Molecular weight	λ_{max}
Yellow		366	356
Red violet		645	532

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