



# Free amino and imino-bridged centres attached to organic chains bonded to structurally ordered silica for dye removal from aqueous solution



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## ARTICLE INFO

### Article history:

Received 4 April 2013

Received in revised form

13 November 2013

Accepted 22 November 2013

Available online 25 December 2013

### Keywords:

Mesoporous silica

Silylating agent

Sorption

Reactive blue dye

## ABSTRACT

Ordered mesoporous SBA-15 type silica was synthesized by sol gel polymerization and reacted with 3-aminopropyltriethoxysilane (AP) or triethylenetetramine (TE), to attach pendant chains or bridging molecules, with basic centres. The materials were characterized by elemental analysis, infrared spectroscopy, and nuclear magnetic resonance in the solid state, X-ray diffractometry, scanning and transmission electron microscopy. The nitrogen sorption/desorption data for SBA-15 and the organofunctionalized SBA-15AP and SBA-15TE silicas resulted in IV type isotherms with hysteresis loops of the H1 type, surface areas of 800; 213 and 457 m<sup>2</sup> g<sup>-1</sup> and average pore diameters of 8.0; 3.2 and 6.8 nm, respectively. The ordered structural features of the mesoporous silica remained preserved after post-functionalization with pendant and bridged organic chains. Sorption data for organofunctionalized silicas gave highly selective sorption capacities for anionic water soluble Reactive Blue dye, with 0.064 and 0.072 mmol g<sup>-1</sup>. Negligible sorption was observed with the unmodified mesoporous silica. The results suggest that organofunctionalized silica can be a simple, efficient, inexpensive and suitable method for the effective and selective removal of anionic organic dye pollutants from aqueous solutions.

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## 1. Introduction

The irreversible industrialization process is one of the major factors that continuously cause damage to the ecosystem. Wastewater discharge without any treatment introduces a set of constituents, mainly those associated with toxic materials such as some organic chemicals, pesticides, dyes and heavy metals, into aqueous systems. These components induce significant disturbances to the environment that can potentially affect aquatic life (Deblonde et al., 2011). Many waste aqueous dyes discharged to the environment produce very serious pollution problems and effects, due to their resistance to degradation under normal conditions (Forgacs et al., 2004). Various kinds of synthetic dyestuffs found in effluents, originating from textile, leather and paper production industries, contain coloured toxic components (Gupta and Suhas, 2009; Acuner and Dilek, 2004) and, therefore, should be removed from any ecosystem. The majority of these dyes contain active azo groups or aromatic rings, which may be

mutagenic and carcinogenic agents (Vanhulle et al., 2008; Baan et al., 2008).

Normally, reactive dyes are highly water soluble, with solubilities varying from 10 to 20% and remain in the wastewater in most manipulation process (Koprivanac et al., 2000). Nearly 50% of these dyes may be lost to the effluents during cellulose fibre dyeing treatments (Netpradit et al., 2004). Taking into account these undesirable effluents in the ecosystem, various conventional handling technologies, such as the tricking filter, activated sludge, chemical coagulation, carbon and zeolite sorptions (Jin et al., 2008; Plekani and Snovink, 2005; Verma et al., 2012; Wang, 2012), photo-degradation processes (Tsui and Chu, 2001), ozonation/fungal treatment (Vanhulle et al., 2008) and also biodegradation (Barragan et al., 2007) have been extensively investigated. Among these known methodologies, sorption is in fact the most effective and economical method for the removal of pollutants from wastewaters (Bakaulah et al., 2007; Cirini, 2006; Dong et al., 2011; Gupta and Suhas, 2009). A relevant aspect to be considered is related to the fact that this process can handle fairly large flow rates, producing high amounts of cleaner effluents and usually does not result in the formation of harmful substances, such as ozone or free radicals, during photo-degradation through ultraviolet light.

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Based on these considerations, the aim of the present study is to investigate removal of organic pollutants from effluents using synthetic mesoporous silica, which has been regarded as an effective sorbent with the advantages associated with high surface area, large diameter and volume, functionalized pore channels and narrow pore size distribution (Rasalingam et al., 2013; Joo et al., 2009).

The presence of inherent silanol groups and the incorporation of amine groups chemically bonded to the polymeric inorganic structure can favour dye interactions (Aguado et al., 2009). The synthesis of ordered mesoporous silica and the associated structural features provides favourable conditions to yield compounds for a variety of useful applications (Gómez-Cazalilla et al., 2007).

This investigation reports the sorption processes of Reactive Blue-15 dye (RB) onto mesoporous silica chemically reacted with silylating agents containing amino groups or as imine bridges attached to covalently bonded chains. The batch sorption process was examined in order to explore the relationship between the efficiency and consequent features related to a structure that can potentially affect the sorption process. The data were adjusted to the Langmuir, Freundlich and Sips models. The obtained kinetic data can elucidate the rate of sorption of the chosen dye on these well-structured mesoporous silicas.

## 2. Materials and methods

### 2.1. Reagents

All reagents and solvents were of analytical grade, 3-aminopropyltriethoxysilane (AP), 3-chloropropyltriethoxysilane (CIP), tetraethylorthosilicate (TEOS), triethylenetetramine (TE), triethylamine; co-block polymer Pluronic P<sub>123</sub> and Reactive Blue-15 (RB), ethanol, xylene, hydrochloric acid. Deionised water was utilized throughout the experiments.

### 2.2. Syntheses of mesoporous silicas

The mesoporous silica SBA-15 was synthesized as previously reported (Zhao et al., 1998). Briefly, 2.0 g of surfactant polymer Pluronic P<sub>123</sub> was dissolved in 12.0 cm<sup>3</sup> of deionised water at 313 K, followed by addition of 60.0 cm<sup>3</sup> of 2.0 mol dm<sup>-3</sup> HCl and the solution was stirred for 2–4 h. After stirring, 4.0 g of TEOS was added and the mixture was stirred during further 4 h. The resultant suspension was kept in an autoclave for crystallization for 24 h at 373 K, under static conditions in a polypropylene bottle. The suspension was filtered, washed with deionized water and dried at room temperature. The excess of surfactant was removed by calcination at 873 K for 6 h.

The synthesized precursor SBA-15 was grafted with 3-aminopropyltriethoxysilane with the purpose to incorporate pendant chains containing attached amino groups. In attempting to get a more effective reaction, an excess of four times of the silylating agent was used in relation to the original silica. Thus, for 1.0 g of the calcinated SBA-15 that contains nearly 8 mmol of OH groups, 37.0 mmol of AP were added. The reaction was performed in 50 cm<sup>3</sup> of xylene with 1.0 cm<sup>3</sup> of triethylamine as catalyst for 72 h at 348 K. Alternatively, with the purpose to obtain a bridged polysilsesquioxane 36.0 mmol of CIP and 18.0 mmol of organo-bridged amine (TE) were mixed in 50 cm<sup>3</sup> of ethanol at 323 K. The suspension was stirred for 72 h then transferred to a three-necked round bottom flask containing 1.0 g of calcinated SBA-15 suspended in xylene, following the same procedure. For both syntheses the solids were filtered, washed with water and ethanol and dried under vacuum to yield SBA-15AP and SBA-15TE silicas, respectively.

### 2.3. Characterizations

The amount of the organic fraction directly bonded to the inorganic silica structure was determined through elemental analysis on a Perkin–Elmer PE-2400 instrument. Fourier transform infrared spectra were obtained by accumulating scans on a Bomem MB-series spectrophotometer with KBr pellets, in the 4000–400 cm<sup>-1</sup> range, with an accumulation of 32 scans and 4 cm<sup>-1</sup> of resolution. Nuclear magnetic resonance (NMR) spectra of the solid samples were obtained on a Bruker Advance 3–300 MHz spectrometer at room temperature. For each run approximately 1 g of each solid sample was compacted in 4 mm zirconium oxide rotors and the measurements were obtained at frequencies of 59.63 and 75.47 MHz with a spinning magic angle of 10 MHz, for silicon and carbon atoms, respectively. <sup>29</sup>Si and <sup>13</sup>C CP/MAS spectra were obtained with pulse repetitions of 3 s for both nuclei and contact times of 4 ms. Nitrogen sorption was performed with a Micromeritics ASAP 2000 or Quantachrome Autosorb using nitrogen at 77 K. The samples were degassed for 8 h at 363 K before the determinations. Small angle X-ray analyses were performed using synchrotron light on the D11A-SAXS line with a wavelength of 0.1488 nm. Thermogravimetric curves were performed using thermal balance model 1090 B, under argon, with a flow rate 30 cm<sup>3</sup> s<sup>-1</sup>, from room temperature to 1250 K, with heating rate 0.167 K s<sup>-1</sup>. The dye sorption was monitored by using a Shimadzu Multispec-1501 spectrophotometer. For pH measurements SevenEesy Metter Toledo pH metre was used. To monitor the dye concentration at specific intervals, the mixture was centrifuged at 4000 rpm using a Rotina 38 Hittich Zentrifugen centrifuge. The morphologies of the silicas were observed by scanning electron microscopy (SEM) with JEOL JS 6360-LV while transmission electron microscopy was performed with JEOL FE6 2700 equipment. The zeta potential of samples suspended in aqueous solution was measured using a Malvern Instruments nano series Nano-ZS Zetasizer based on the method of electrophoretic light-scattering that measures the migration rate of dispersed particles under the influence of an electric field. After five series of measurements, the mean value and standard deviation of the zeta potential were obtained.

## 3. Results and discussion

### 3.1. Elemental analysis

The percent of carbon and nitrogen in the anchored chains chemically bonded to the inorganic framework in the elemental analyses are summarized in Table 1. Based on these values the carbon/nitrogen molar ratios were calculated and compared to the expected data. For both synthesized silicas the obtained C/N ratios were slightly higher than expected. These differences may be interpreted as a result of incomplete hydrolysis of the ethoxide groups of the silylating agent or some balance of the surfactant polymer that remains after calcination (Maria Chong and Zhao, 2003). The degree of immobilization of the silylating agent bonded to the inorganic framework can be calculated through Eq (1):

**Table 1**

Percentages (%) of carbon (C) and nitrogen (N), the respective amounts (mmol g<sup>-1</sup>), and calculated (C/N<sub>cal</sub>) and expected (C/N<sub>exp</sub>) carbon/nitrogen molar ratios for SBA-15AP and SBA-15TE silicas (Sil).

Sil	C/%	N/%	C/mmol g <sup>-1</sup>	N/mmol g <sup>-1</sup>	C/N <sub>cal</sub>	C/N <sub>exp</sub>
SBA-15AP	14.89	5.14	12.41	3.67	3.00	3.38
SBA-15TE	11.61	3.41	9.67	2.43	3.00	3.97

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