



# An investigation into the effect of porosities on the adsorption of rhodamine B using titania–silica mixed oxide xerogels



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## ABSTRACT

Aperiodic mesoporous titania–silica ( $\text{TiO}_2\text{-SiO}_2$ ) xerogels with varying silica contents were synthesized under ambient conditions. The physico-chemical properties of the xerogels were examined by a variety of techniques that include powder X-Ray Diffraction (XRD), nitrogen adsorption, Fourier Transform-Infrared spectroscopy (FT-IR), Scanning and Transmission Electron Microscopies (SEM and TEM), Thermo Gravimetric Analysis (TGA), zeta potential, and Diffuse Reflectance Spectroscopic (DRS) studies. The adsorption of a model dye molecule, rhodamine B (RhB) was studied over the titania–silica xerogels and compared with titania and silica. It was determined that the pore volume of the xerogels mainly influences the adsorption of RhB. The xerogels exhibited good adsorption capacity with more than 90% dye removal at low dye concentrations. Our results suggest that low cost approaches to the synthesis of xerogels with tailored properties such as large pore volume could provide cost-effective solutions to mitigate environmental problems related to removal of water based toxic pollutants such as dyes by simple adsorption processes.

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## 1. Introduction

Various methods have been employed for the removal of dyes and pigments to minimize water pollution from the uncontrolled dumping of waste effluents by the textile industry. Chemical techniques such as electro-oxidation, coagulation, and flocculation are often expensive and extremely sensitive to several experimental conditions and in addition, may cause undesirable secondary pollution due to excessive usage of chemicals (Huang et al., 2011; Wang and Chu, 2011). Hence, economically affordable and environment friendly avenues need to be explored.

Adsorption is one of the most promising physical means for industrial remediation applications, in particular for water purification. Extensive literature has been reported regarding dye removal from aqueous solutions by using a myriad of adsorbents derived from clay minerals (Khan et al., 2004), activated carbon (Annadurai et al., 2001; Pelekani and Snoeyink, 2000; Ramuthai et al., 2009), coal (Mohan et al., 2002b), wood (Garg et al., 2003), carbon xerogels (Figueiredo et al., 2011), fly ash (Lin et al., 2008; Mohan et al., 2002a; Shaobin et al., 2005), and bio-materials (Debrassi and Rodrigues, 2011; Hii et al., 2009). However, owing to the lack of effective adsorbate–adsorbent interactions, which

can be ascribed either to the relatively limited surface area or clogged “dead volume” in the pores of adsorbents, a number of the above mentioned materials are found to be sluggish for the adsorption of dyes. Thus, only moderate adsorption capacity can be achieved in some of these adsorbents.

Oxides constitute an important class of adsorbents, and in this regard, silica gels (Tada et al., 1998; Alemany et al., 1997), zeolites (Xu and Langford, 1997),  $\text{Al}_2\text{O}_3$  (Desai et al., 1997),  $\text{SiO}_2$  (Anderson and Bard, 1997; Chen et al., 2003), and  $\text{TiO}_2$  (Belessi et al., 2009; Bourikas et al., 2005; Fetterolf et al., 2003; Jafari et al., 2011; Lee et al., 2011), have been examined as adsorbents for removal of dyes. Among these oxide materials, titanium dioxide is an important material that finds applications in heterogeneous photocatalysis for splitting of water, degradation of pollutants, and solar cell applications. One method to improve the activity of titania is to generate highly porous structures with large surface areas that will provide materials with greater number of active sites per gram of material and also promote effective transport of reactants and products to the active site(s). This has been demonstrated by preparing mixed metal oxides. Among the various mixed oxides, titania–silica has garnered the close attention of several researchers (Brodzik et al., 2008; Davis and Liu, 1997). A comprehensive review related to the use of titania–silica materials as catalysts has been reported by us recently (Kibombo et al., 2012). It has been suggested that the photocatalytic decomposition of dyes such as Rhodamine 6G (R-6G) is increased due to its enhanced

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adsorption because of the presence of SiO<sub>2</sub> (Anderson and Bard, 1997). Previous results indicate that titania supported siliceous materials show higher activity compared to titania due to enhanced concentration of organics on the photocatalyst surface, however it was also noted that enhanced adsorption is not the only requirement for higher photocatalytic activity (Anderson and Bard, 1997; Xu and Langford, 1997).

The adsorption capacity of an adsorbent is governed by several factors that include surface area, surface charge, number (density) of surface hydroxyl groups, pore size, pore volume, and pore shape (geometry) (Pelekani and Snoeyink, 2000, 2001). In addition, it has been widely reckoned that the surface properties can be tuned by elaborate control of the synthetic method. Sol–gel chemistry is a common method for the synthesis of titania–silica mixed oxides and was hence employed in this work (Brinker and Scherer, 1990; Mikushina et al., 2008; Pirson et al., 1995). Enhancement of morphological features of such materials has been attempted by using hydrothermal and supercritical drying techniques. However, these energy intensive procedures require either extra processing steps or the use of elaborate high pressure equipment such as autoclaves and furnaces at additional cost (Anderson and Bard, 1995; Dutoit et al., 1996; Hench and West, 1990). A less energy intensive method for the preparation of oxide materials is by drying the solvent under ambient conditions to produce xerogels. Several synthetic procedures have been reported for their preparation, but the most common methods usually result in non-porous materials (Erdem et al., 2001; Fernandez et al., 2007; Handy et al., 1992; Holland et al., 2000; Lorret et al., 2006). This is because the drying of the solvents under ambient conditions cause collapse of the pores due to the differential capillary pressure developed. The pressure gradient is created due to the different rates of evaporation of the solvent from the various pores. One method to prevent the collapse of the pores is by using non-polar solvents in the synthesis gel. TiO<sub>2</sub>·SiO<sub>2</sub> xerogels (containing equimolar ratios of TiO<sub>2</sub> and SiO<sub>2</sub>) were synthesized by using co-solvent induced gelation (CIG) at ambient conditions developed by us previously (Budhi et al., 2011). The non-polar solvent, toluene used in this method, helps not only to enhance the gelation process but also assists in the formation of mixed oxides with enhanced porosities.

To our knowledge, a systematic study that elucidates the role of silica component in modulating the textural properties of binary aperiodic mixed metal oxides is lacking in the literature. Although, the photocatalytic degradation of organics by using TiO<sub>2</sub>·SiO<sub>2</sub> mixed oxide materials have been explored in literature, a thorough physico-chemical characterization of these binary mixed oxide to probe the factors influencing adsorption is missing. Therefore, the aim of this work is to investigate the effect of SiO<sub>2</sub> content on the textural properties of TiO<sub>2</sub>·SiO<sub>2</sub> mixed oxides by intentional and rational adjustment of the SiO<sub>2</sub> amount. Subsequently, the prepared TiO<sub>2</sub>·SiO<sub>2</sub> samples were utilized as adsorbents to examine their adsorption efficiencies toward removal of potentially hazardous Rhodamine B (RhB) dye from aqueous solution.

Thus, this work is the first report of systematic and detailed investigation of aperiodic TiO<sub>2</sub>·SiO<sub>2</sub> mesoporous materials prepared by facile and economic sol–gel synthesis toward the application of removal of RhB dye from aqueous solutions. We were able to obtain TiO<sub>2</sub>·SiO<sub>2</sub> materials with distinct textural properties, by tuning the TiO<sub>2</sub>:SiO<sub>2</sub> ratios in the synthesis gel. The adsorption capacity of TiO<sub>2</sub>·SiO<sub>2</sub> materials for RhB exhibits a strong correlation with their pore volumes. TiO<sub>2</sub>·SiO<sub>2</sub> mixed oxides significantly promoted the adsorption of RhB onto its surface and this provides a prospective view for these materials to act as effective photocatalysts for de-coloration of RhB under assistance of visible light, which is, however, beyond the scope of this work. We also note that, the surface environment (surface area, surface charge, and

surface hydroxyl groups) of TiO<sub>2</sub>·SiO<sub>2</sub> materials are found to have only moderate contribution to the adsorption behavior. All of the prepared samples were thoroughly characterized via various techniques including powder XRD, nitrogen physisorption, Scanning and Transmission Electron Microscopy (SEM and TEM), Thermo Gravimetric Analysis (TGA), Fourier Transform Infra-Red spectroscopy (FT-IR), and zeta potential measurement.

## 2. Experimental methods

### 2.1. Materials

Tetraethylorthosilicate (TEOS, Acros 98%), titanium isopropoxide (Ti(<sup>i</sup>OPr)<sub>4</sub>, Acros 98+%), ethanol (Pharmco-AAPER, ACS/USP grade, 200 proof), toluene, conc. nitric acid (HNO<sub>3</sub>) (all ACS grade) were used as received for the preparation of the TiO<sub>2</sub>·SiO<sub>2</sub> xerogel adsorbents. Without further purification Rhodamine B, (RhB, Alfa Aesar) was employed as a model organic dye, and deionized water (resistivity > 18 Ω cm) was used to prepare the solution mixtures.

### 2.2. Synthesis of TiO<sub>2</sub>·SiO<sub>2</sub> xerogels

TiO<sub>2</sub>·SiO<sub>2</sub> xerogels were prepared by mixing 9 mL of ethanol, 9 mL of co-solvent toluene, 1.65 mL (7.4 mmol) of TEOS, 1 mL (55.55 mmol) of water, and 0.25 mL (5.6 mmol) of conc. HNO<sub>3</sub> in a plastic beaker at room temperature. Finally, 2.2 mL (7.4 mmol) of Ti(<sup>i</sup>OPr)<sub>4</sub> was added drop-wise with stirring at 300 rpm to obtain a TiO<sub>2</sub>:SiO<sub>2</sub> molar ratio of 1:1. The stirring was discontinued when the reaction mixture formed a clear gel typically within the range of few minutes to a few hours. The gel was then kept for drying at room temperature and the duration (1–2 weeks) was determined to be dependent on the amount and nature of the co-solvent. The TiO<sub>2</sub>:SiO<sub>2</sub> molar ratios were varied by using appropriate amounts of Ti(<sup>i</sup>OPr)<sub>4</sub> and TEOS. After drying, the xerogel was transferred to an oven maintained at 80 ± 10 °C overnight. The dry solid powder obtained was crushed and calcined by heating in static air at 550 °C for 6 h prior to characterization. The resultant mixed oxides are labeled X-TiSi to denote xerogels–titania–silica and the subsequent numbers are arbitrary in chronological order for the sake of clarity.

### 2.3. Characterization

The structural features of the calcined xerogels were examined by using different characterization techniques. Powder X-ray diffraction patterns were recorded at room temperature on a Rigaku Ultima IV instrument with Cu Kα radiation (λ = 1.5408 Å) at an accelerating voltage of 40 kV and current of 44 mA. The powders were scanned from 10 to 80° (2θ) with a step size of 0.02° and scan rate of 1°/min., and the diffraction patterns obtained were analyzed using PDXL software provided by Rigaku. Nitrogen physisorption studies were carried out using Quantachrome NOVA 2200e surface area analyzer. The Brunauer–Emmett–Teller (BET) equation was used for calculation of the surface area in the relative pressure range (P/P<sub>0</sub>) of 0.05–0.30. The pore volume was calculated from the amount of nitrogen adsorbed at the highest relative pressure of P/P<sub>0</sub> ~ 0.99. The Barrett–Joyner–Halenda (BJH) equation was used to calculate the pore diameter from the desorption isotherm. The samples were dried overnight in an oven at 80–90 °C and further extensive degassing was done at 100–120 °C prior to the N<sub>2</sub> adsorption measurements. Deducing from various studies of such mixed oxides, these degassing conditions have emerged sufficient since our materials do not retain excess amounts of solvent as confirmed by thermogravimetric analysis (TGA). High magnification images were recorded on a Hitachi H-7000 FA Transmission Electron Microscope (TEM) operating at 100 kV. The samples

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