Effect of the amount and time of addition of a dye template on the adsorption and photocatalytic performance of molecularly imprinted silica

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ABSTRACT

A molecularly imprinted (MI) photocatalyst was prepared via an acid-catalyzed sol-gel route using Rhodamine B (RhB) as the template. The aim of this study was to evaluate the effect of the amount and time of addition of RhB on the photocatalytic degradation. The adsorption kinetics of MI silica xerogels were also investigated. Several methods of extraction were employed, and the use of ultrasound (in methanol) exhibited the best results with respect to increasing the surface area, template removal and economy of spent solvent volume. The samples were characterized in terms of their pore diameter, surface area and aggregation of primary particles using small-angle X-ray scattering. For systems containing a fixed mass of template (150 mg), the textural evidence suggests that the large pores and large surface areas may explain the improved results that were achieved by systems where the template was added at t = 0. In addition, the effect of the added template amount at a fixed time indicated that there is a threshold at which degradation was improved. The results suggest that using a higher template content in the synthesis of the photocatalysts may hinder removal from the silica network and increase the aggregation of molecules, affecting the photocatalytic performance.

1. Introduction

Synthetic dyes have become an integral component for a variety applications. The majority of these dyes (ca. 70%) belong to the azo group [1]. Approximately 7×10^5 metric tons of dye are produced annually [2] for various applications, such as the plastic, textile, printing and cosmetic. Some estimation suggests that for 1 kg of textile materials the textile finishing industries consume 100 L of water [4]. Such consume is partially a consequence of textile industry, from which it is estimated that each year ca. 2.8×10^5 tons of dyes are discharged [5]

These discharged possibly affect the aquatic life by hindering sunlight penetration in water. Therefore, removing these dyes from wastewater remains a difficult challenge, especially the removal of dyes at a low concentration [6].

Chemical treatment, filtration, oxidation, adsorption, biological treatment and advanced oxidation processing, are among the most commons methods available for remediation of dye wastewaters [3,7]. However, a condition that is necessary for complete removal is the mineralization of the contaminant [8], which can be achieved by using advanced oxidation processes (AOPs).

Considering emerging contaminants, the heterogeneous photocatalysis is one of more promising strategies among AOPs. The use of TiO_2 as catalyst encompasses several advantages, such as low cost and low toxicity [9]. However, the low selectivity to most hazardous compounds is a serious disadvantage of heterogeneous photocatalytic oxidation [10,11].

To address this drawback, some studies have suggested combining molecularly imprinted (MI) technology with a photocatalytic process. One of its main feature is that MI technology demonstrates high affinity and selectivity for the molecules employed as templates [12,13]. In this approach, the cavities generated by MI technology could enhance the molecular recognition ability. MI materials have been used in many different applications, such as drug delivery [14], catalysis [15], adsorption [16–18], chemical sensing [19], preconcentration [20], biological antibodies, and receptor systems [21].

The production of MI as sorbent material is majority based on organic matrix. However, the adsorption sites generated are usually heterogeneous and also possess non-specific interactions between the template and the imprinted sites that compromise the adsorption phenomenon [22]. In order to overcoming these inconveniences, a promising alternative is the use of inorganic matrices, such as silica-based material.

Silica-based imprinted materials can be produced by sol-gel process.

Briefly, a precursor (e.g., tetraethylorthosilicate (TEOS)) interacts with a chosen template producing a silica network. After the extraction of the template, specific cavities are created and the produced material can be used as an adsorbent. As shown in the literature [23,24], the main advantage of silica prepared by sol-gel reactions is that material can be tolerant to a several chemical environments [25], which include exposure to very strong base, very strong acid, and oxidizer species. Silica materials as adsorbents in solid-phase for drug extraction are among the majority of the studies discussing the preparation of silica material containing molecularly imprinting technology [26–28].

Imprinted photocatalysts based on inorganic matrix have not yet been extensively explored in the literature [29–33]. In this context, the aim of the current study was to evaluate the effect of the amount and time of addition of a template (RhB) on the characteristics and catalyst activity of a photocatalyst that was prepared via an acid-catalyzed sol-gel route. Different extraction methods were studied and, after selecting the best extraction method, the adsorption kinetics of the MI xerogels (without calcination) were investigated.

2. Experimental section

2.1. Materials and methods

Tetraethoxysilane (Si(OCH$_2$CH$_3$)$_4$, TEOS, Merck, > 98%), Rhodamine B (Vetec), and titanium tetrachloride (TiCl$_4$, Merck, > 99%) were used as received. Hydrochloric acid (HCl, Nuclear, 38%) was employed as the catalyst.

2.2. Preparation of sol-gel materials

The photocatalysts were prepared using a sol-gel process using HCl (0.2 M) as the catalyst. TEOS (45 mmol) was used as the raw material at a 1:2 (HCl:TEOS) volume ratio followed by the addition of TiCl$_4$ (10.4 mmol). The effect of the amount of template was investigated by adding 150, 300 and 500 mg of RhB at the start of the reaction. The effect of the time of template addition was evaluated by fixing the amount of RhB at 150 mg with the addition occurring t = 0, 60, 90 and 120 min after starting the sol-gel reaction.

After the preparation of silica containing encapsulated dye, the next step was the template removal. Three extraction methods were investigated: ultrasound, Soxhlet and solvent washing. Methanol as solvent was chosen for Soxhlet and ultrasound-assisted (Branson-Sonifer®, 250 W) extraction. In the washing process, deionized water was used.

Prior to the photocatalytic process, the samples were heated to form the photoactive phases (i.e., anatase and rutile). The samples were submitted to two different heating processes until 450 °C as described elsewhere in our previously publication [31]. The first was submitted to a heating rate of 5 °C/min (15C0*) and the second approach was with a heating rate of 1 °C/min (15C0). This procedure was continued to 450 °C, and then the sample was kept in this temperature 4 h, which was chosen based on minimum time needed for the formation of photoactive phases [34]. Finally, the material was rinsed with deionized water to remove any residue and dried at 80 °C.

The samples were labeled according to the amount and time at which the template was added as well as the stage of preparation. Therefore, **A** refers to systems extracted but non-calcined, and **C** refers to systems extracted and calcined. For example, 15C120 corresponds to 150 mg of template added at t = 120 min after the sol-gel reaction was initiated, and 50C0 corresponds to addition of the template at t = 0 min and 50 mg of RhB.

2.3. Instrumentation and Characterization

The specific surface area and pore diameter were determined in a Gemini 2375 Micrometric apparatus. More details can be found elsewhere in our previous publication [17,31].

The carbon and nitrogen content was determined in a Perkin-Elmer (Wellesley, MA, USA) M-CHNSO/2400 analyzer.

The small-angle X-ray scattering (SAXS) experiments were performed on the D11A beamline at the Brazilian Synchrotron Light Laboratory (LNLS, Brazil). Igor Pro Software (WaveMetrics, Portland, USA) [35] was used for the implementation of the Irena routine that was used for processing the data [36]. More details can be found elsewhere [17,31].

For photocatalytic essays, modified mercury vapor lamp (Philips HPL-N 125 W) emitting only UV-A (365 nm) was used. Previously to each experiment, the UV-radiation radiation was adjusted using a Radiometer Series 9811 (Cole-Parmer Instruments) by using an Hg vapor lamp (125 W). Centrifugation was carried out using a Cientec CT-5000R.

Spearman between the data was analyzed using SPSS Statistical System (SPSS for Windows, version 19, IBM® and were performed at a P < 0.05 level of significance.

2.4. Adsorption and photocatalyst evaluation

In the adsorption experiments, 10 mg of RhB-imprinted silica were introduced into a cartridge at 25 °C through which 5 mL of RhB solution (20 ppm) was percolated over 360 min.

Photocatalytic tests were performed using 0.6 g/L of the photocatalyst in a bath reactor which details were given in a previous study [31]. 50 mL of RhB (20 ppm) was kept under flowing air and keeping the temperature reaction at 30 °C during 1 h under a UV-light. Prior to each experiment, the UV-radiation was adjusted to 45 W m^{-2}. The tests were carried out at natural pH (i.e., 4.7).

For both adsorption and photocatalytic tests, the samples were collected at regular intervals for further centrifugation (4,000 rpm) and the concentration was determined using UV-visible spectrometry at 553 nm. The reported results are the mean values of triplicates.

Adsorption and degradation were estimated from the calibration curve shown in Eq. (1)

$$A_{RhB} = 0.21.C_{RhB} + 0.03, \ N = 7, \ R^2 = 0.996 \tag{1}$$

where A is absorbance value and C is the concentration (mg/L) from Eq. (2) that was employed to calculate adsorption and degradation degrees,

$$\text{Adsorption or Concentration}(\%) = \frac{\text{Ci-Cf}}{\text{Ci}} \times 100\% \tag{2}$$

Where Ci and Cf are the initial and final concentration (mg/L), respectively.

3. Results and Discussion

3.1. Xerogel and Photocatalysts Characterization

Table 1 shows the C and N content, the S$_{BET}$ values and the solvent volume used for the different extraction methods for the 15A0 system (non-calcined). Although a decrease in the C content was observed compared to that in encapsulated silica, the carbon content can be misleading due to the potential presence of residual ethoxide groups in silica that are produced by the sol-gel method [37].

According to Table 1, the highest removal of N was obtained using thermal extraction. However, no increase in the area was achieved, suggesting that the silica may have collapsed. Similar results have been observed after thermal extraction of paracetamol from a silica network [37].

By comparing the extractions using solvents, the extraction by ultrasound required nearly 9 times less solvent than that required in the washing protocol and 6 times less solvent compared to that used in the Soxhlet protocol. In addition, ultrasonic extraction with methanol resulted in the lowest solvent consumption as well as the lowest solvent volume/increase in S$_{BET}$ ratio. By comparing the extraction performed