

The sol–gel route effect on the preparation of molecularly imprinted silica-based materials for selective and competitive photocatalysis



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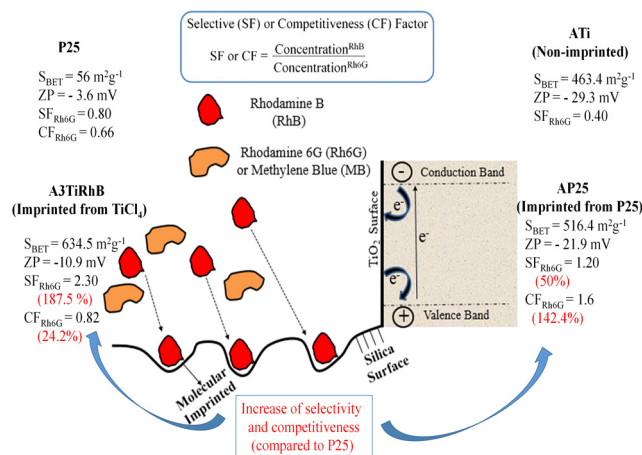
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HIGHLIGHTS

- A series of molecularly imprinted photocatalysts were prepared by sol–gel routes.
- Photocatalytic tests were conducted to evaluate the selectivity and competitiveness.
- Adsorption occurs on the domains of silica imprinted.
- An increase in selectivity was obtained (up to 2.8-fold) compared to the P25.
- An increase in competitiveness was obtained (up to 55%) compared to the P25.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of molecularly imprinted photocatalysts containing rhodamine B (RhB) as a template were prepared from four different routes, namely acid, basic-catalyzed, two-steps and non-hydrolytic sol–gel routes, using TiCl_4 as a TiO_2 source. Variations in acid route synthesis (rate of heat on calcination, absence of HCl and replacement of TiCl_4 for commercial P25) were also evaluated. For comparison, non-imprinted samples were also synthesized. Photocatalytic tests were conducted to evaluate the selectivity (RhB, rhodamine 6G (Rh6G) and methylene blue (MB)), competitiveness (RhB versus Rh6G and RhB versus MB) and regeneration of catalysts in terms of initial adsorption and degradation. The effects of the solid photocatalyst texture and structure (surface area, zeta potential, radius of gyration and fractal geometry) on the degree of RhB degradation were also examined. From the results of the photocatalysis tests and statistical analysis, we have shown that dye adsorption occurs on the silica domains that are imprinted in the vicinity of the photocatalyst due to photocatalytic degradation. Compared to the commercial photocatalyst (P25), an increase in selectivity (up to 180%) and competitiveness (up to 290%) were obtained. Regarding the acid route, the absence of HCl during the catalyst synthesis resulted in a loss of degradation compared to P25 and a 3-fold lower factor of competitiveness compared to the system in which HCl was used. In the regeneration tests, degradation was maintained at 80% of that of initial tests for up to three cycles.

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1. Introduction

Advanced oxidation processes (AOPs) are known methods of pollutant degradation that involve mineralization of a wide variety of organic contaminants. Among the compounds of concern, there are emerging contaminants, that include pharmaceutical and personal care products, steroids, surfactants, pesticides and dyes [1]. In the case of synthetic dyes, it is estimated that more than 280,000 tons are discarded worldwide [2]. Many of these contaminants are not adequately removed in conventional treatment processes. In these cases, mineralization, or the conversion of the molecules to their highest possible oxidation state and then into water, carbon dioxide, oxidized inorganic anions and/or other molecules that can be removed by biological processes, is required for full removal.

Among the AOPs, heterogeneous photocatalysis using TiO_2 is one of the most promising for use with emerging contaminants. Although this method shows clear advantages, such as low cost, low toxicity and chemical stability [3], heterogeneous photocatalysis lacks selectivity for the most hazardous contaminants [4,5]. This characteristic is a disadvantage, as mixtures derived from effluent streams may contain hazardous contaminants and low toxicity contaminants. In many cases, the former is present in lower concentrations, and the latter is the majority [4,5], but it is desirable to preferentially degrade the most toxic materials.

The commercial use of TiO_2 is also difficult due the cost of separating the treated effluent and the photoactive micro-particles. One possible method to overcome this challenge is to the use of supports [6], which provides other advantages, including immobilization of the active catalyst, increases in the catalytic material surface area, and improvements in thermal and chemical stability [7]. Thus, several studies have explored different uses of supports, such as activated carbon, clay, graphene and zeolites [8–11].

Although extensively studied, the use of supports in heterogeneous photocatalysis does not necessarily address the problem of selectivity. Therefore, a new approach has been investigated here that combines the technique of molecular imprinting (MI) with heterogeneous photocatalysis. MI is a promising technique for creating a template of specific molecular recognition [12]. This technique can be carried out in an organic or inorganic matrix due to the presence of a template molecule during the formation of the three-dimensional polymer [13,14]. The majority of MI applications in inorganic matrix materials are based on a silica network that is synthesized by the sol–gel method. Recent studies have shown the feasibility of this approach for selective adsorption and pre-concentration of compounds such as drugs and dyes [15,16].

The imprinting approach combined with photocatalysis is very promising due to its simplicity. However, among the studies that have been conducted on this approach [5], the majority of them have utilized an organic matrix. Thus, the effect of MI in inorganic matrices on selective photocatalysis is not well understood. We have previously investigated the effect of the sol–gel route in molecularly imprinted materials in terms of textural and structural properties. We have shown the potential of silica imprinted materials for use in selective adsorption, and we have demonstrated that Ti moieties (using TiCl_4 as a source of TiO_2) can be incorporated into the silica network [16,17]. We also have discussed adsorption capacity (q_m) for RhB in terms of isotherm adsorption for different sol–gel routes [18]. We have shown that acid-catalyzed route yielded a q_m value of 998.3 mg g^{-1} (Langmuir model), which is comparable or even higher than the recent reports. Taking into consideration, we were motivated to explore different methodologies (comparing TiCl_4 and P25 as precursor to TiO_2) to prepare photocatalysis based on acid-route. As an extension of these studies, the present work reports on the effect of the sol–gel route on preparation of photocatalysts for selective and competitive photocatalysis. The effects of textural characteristics (surface area, zeta

potential, radius of gyration and fractal geometry) on RhB degradation are also discussed. To the best of our knowledge, the current work is the first report on the influence of material sol–gel routes on heterogeneous selective and competitive photocatalysis.

2. Experimental

2.1. Materials and methods

Rhodamine B (RhB) (Vetec), rhodamine 6G (Rh6B) (Sigma–Aldrich), methylene blue (MB) (Vetec), tetraethoxysilane ($\text{Si}(\text{OCH}_2\text{CH}_3)_4$, TEOS, Merck, >98%), titanium tetrachloride (Merck, >99%), silicon tetrachloride (SiCl_4 , Sigma–Aldrich, 99%) and titanium dioxide (TiO_2 , P25–Degussa) were used as received. Hydrochloric acid (HCl, Nuclear, 38%), ammonium hydroxide (NH_4OH , Nuclear, 29%) and FeCl_3 (98%, Merck) were employed as catalysts.

2.2. Preparation of the photocatalysts

Five different routes were employed to prepare the samples using the sol–gel process and TEOS as the raw material. The routes were labeled as follows: acid-catalyzed route 1 (A1), acid-catalyzed route 2 (A2), base-catalyzed route (B), two-step route (TS) and non-hydrolytic route (NH). Acid-catalyzed route 1 utilized 0.2 M hydrochloric acid at a 1:2 (HCl:TEOS) ratio. Acid-catalyzed route 2 was similar to acid-catalyzed route 1, but the samples were prepared without hydrochloric acid (i.e., TiCl_4 acted as a potential Lewis acid catalyst). The base-catalyzed route utilized 0.2 M ammonium hydroxide at a 1:2 (NH_4OH :TEOS) ratio. The two-step route utilized 0.2 M hydrochloric acid at a 1:2 (HCl:TEOS) ratio; then, after 30 min., 0.2 M ammonium hydroxide was added at a 1:2 (NH_4OH :TEOS) ratio. The non-hydrolytic route employed TEOS and SiCl_4 and was catalyzed with FeCl_3 (0.5 wt.% of the final product weight). For each sample, RhB was fixed at 150 mg.

Samples (powder) from the acid-catalyzed, base-catalyzed and two-step routes were prepared as follows. RhB was added to a solution of TEOS followed by addition of TiCl_4 , and then the catalyst was added. During this process, the solution was continuously stirred at room temperature until gelation or precipitation occurred, depending on the route. For the non-hydrolytic route, the procedures were executed under inert atmosphere (Ar). TEOS, SiCl_4 and TiCl_4 were added after adding the catalysts and RhB. The resulting solution was stirred at 80°C until gelation. The solids were dried at room temperature and milled.

For template removal, ultrasound-assisted (Branson-Sonifer[®], Model 250) extraction was employed using methanol as the solvent (approximately 70 mL). The process was conducted by altering modes of pulse-on (20 s) and pulse-off (5 s) for five minutes. The solid was filtered and dried at room temperature. These samples were labeled molecularly imprinted (MI). For all of the routes, equivalent synthesized samples were prepared without the addition of RhB, i.e., non-imprinted (NI) systems.

MI and NI systems were submitted to a calcination process. This process was carried out in a muffle furnace at 450°C for 4 h at a rate of $5^\circ\text{C}/\text{min}$. For acid route 1, the effect of heating rate was also evaluated. In this case, the system was labeled as acid route 3 (A3), in which calcination occurred slowly by keeping the temperature constant for 1 h at each increment of 100°C and by utilizing a heating rate of $1^\circ\text{C}/\text{min}$. This procedure was continued until the temperature reached 450°C , and then the material was held at this temperature for 4 h.

In order to combine the concept of molecular imprinting with photocatalyst impregnation, acid route was also evaluated by replacing TiCl_4 with P25 (Degussa). In this case, P25 was added 2 ½ h after

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