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TiO_2 soportada en partículas magnéticas para la degradación de tartrazina

Tartrazine degradation by supported TiO_2 on magnetic particles

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RESUMEN

En el presente trabajo se han obtenido perlas magnéticas mediante la adición de una solución de alginato de sodio conteniendo partículas de magnetita a una solución de $CaCl_2$, las cuáles fueron utilizadas como soporte de TiO_2. Las partículas de TiO_2 en fase anatasa, obtenidas por el método sol-gel a baja temperatura (75 °C), fueron soportadas en las perlas magnéticas para obtener el fotocatalizador magnético, CM. La superficie específica BET del núcleo de magnetita y el fotocatalizador magnético fueron obtenidas por adsorción de N_2, la morfología de las partículas fueron observadas por microscopía electrónica de barrido (SEM) y la fase TiO_2 fue analizada mediante espectroscopía Raman. La actividad fotocatalítica de CM fue evaluada en la degradación del colorante tartrazina, muy utilizado en la industria alimenticia, a dos concentraciones diferentes. Finalmente, la estabilidad del catalizador fue evaluada mediante ensayos de la re-usabilidad en varios ciclos posteriores. Los resultados mostraron que la fase anatasa soportada en las partículas magnéticas presentan buena actividad fotocatalítica en la de degradación de tartrazina, principalmente cuando la concentración del colorante es baja, y que pueden ser fácilmente recuperados y re-utilizados en varios ciclos con una moderada pérdida en la eficiencia fotocatalítica.

Palabras clave: TiO_2 soportado, perlas magnéticas, degradación de tartrazina.

ABSTRACT

Magnetic beads were obtained by dropping a solution of sodium alginate containing magnetite particles into a $CaCl_2$ solution. TiO_2 anatase particles were synthetized by a sol-gel method at low temperature (75 °C), and were supported on magnetic beads to obtain the magnetic photocatalyst, MC. Magnetite particles and magnetic photocatalyst were characterized by nitrogen adsorption (BET, surface area), their morphology observed by scanning electronic microscopy (SEM) and TiO_2 phase was analyzed by means of Raman spectroscopy. The photocatalytic activity of MC was evaluated on tartrazine degradation, highly used in food industry, at two different concentrations. Finally, MC stability was evaluated by reusability assays in several subsequent cycles. Results showed a good photocatalytic response for tartrazine degradation, especially at low concentration, easy recuperation and appropriate perform in the reusability of MC.

Keywords: supported TiO_2, magnetic beads, tartrazine degradation.

1. INTRODUCTION

Heterogeneous photocatalysis using semiconductor TiO_2 is widely used in environmental decontamination, such as air purification or removal of organic and inorganic pollutants from waste waters. The TiO_2 photocatalyst shows attractive optical and electronic properties, high photocatalytic activity and chemical stability

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and non-toxicity. TiO_2 presents three crystalline phases, anatase, rutile and brookite, being anatase the most important in photocatalysis [1-4]. However, its particle sizes have limited practical application in suspension mainly because of its costs of separation. To overcome this problem, titania has been immobilized on several materials such as glass, ceramic and zeolites [5-8]. The photocatalytic activity of supported titania is considerably reduced because the effective surface area exposed in the supported systems is also decreased.

Magnetic particles, such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), have been studied for potentials applications, especially in bioengineering and biomedicine areas [9-10]. They had demonstrated to be a good alternative to be used as supports of TiO_2 particles, since they can be easily be separated from the solution by application of a magnetic field. Nevertheless, previous studies have demonstrated that direct deposition of titania on magnetic cores produce a critical decrease of photoactivity [11-12]. This behavior was related with the formation of strong chemical interactions between iron oxide and titanium oxide phases that take place during the heat treatment used to develop anatasa phase, which modifies both photoactivity and magnetic properties [11-12].

On the other hand, magnetic particles have been stabilized by incorporation of interphase between magnetite and anatase phases, principally SiO_2 matrix. This interphase has been demonstrated to be an excellent option to insulate the iron oxide [13-17]. Moreover, other polymers have been studied to encapsulate Fe_3O_4 nanoparticles for different applications [18-19]. Particularly, sodium alginate which is an economical and no-toxic polysaccharide has been applied to drug delivery [20-21] and adsorption of pollutant in waste water [22], but there are limited applications in photocatalysis [23-24].

In the present work, we synthetized a TiO_2 photocatalyst supported on magnetic beads obtained by encapsulation of magnetite particles in alginate matrix. The anatasa TiO_2 phase was obtained by sol-gel method at low temperature (75 °C). Its photoactivity was evaluated in degradation of azo-acidic tartrazine dye, which is often used to provide orange coloring to foods, drinks and pharmacological products. Tatrazine has been implicated as the food additive, most often responsible for allergic reactions, having thus been targeted by the scientific community. Some authors have studied the carcinogenetic and mutogenetic effects of tartrazine with variable results [25-26]. In spite of these health concerns, there are currently only a few studies of tartrazine degradation by heterogeneous photocatalysis [27].

2. EXPERIMENTAL

2.1 Synthesis of magnetic photocatalyst

The magnetic beads were obtained by entrapping Fe_3O_4 nanoparticles in the matrix of sodium alginate. Nanoparticles of commercial magnetite, provided by Alfa Aesar, were dispersed in 20 mL of sodium alginate solution at 2% m/v, in an ultrasonic bath for 30 min. The resultant suspension or “magnetic ferrofluid” was added dropwise in a solution of calcium chloride at 2% m/v, using a syringe. Magnetic beads were maintained in the calcium bath overnight, so that the gelation reaction had enough time to be carried out in the whole volume of the bead. After the curing period, the beads were removed from the $CaCl_2$ solution, washed several times with distilled water and kept in a distilled water bath to remove the maximum amount of unbounded calcium.

On the other hand, anatase TiO_2 nanoparticles were prepared by the sol-gel method at low temperature using a previously reported method [30]. Briefly, 20 mL of water at pH = 2 (adjusted with HNO_3) were added to 10 mL of 1M solution of titanium tetraisopropoxide (TTIP, by Aldrich 97%) in isopropyl alcohol (Ciccarelli P.A) under continuous stirring. A white sol was instantly obtained and was aged keeping it under reflux condition at 75 ºC for 5 h. This time was previously determined as the optimal time to promote the anatase crystalline phase formation [30].

Finally, magnetic wet cores were added to titania sol in ultrasonic bath for 1 hour and then, they were totally dried in a rotary evaporator under vacuum (near 5.0 x 10^{-4} mbar) to obtain the magnetic catalyst, MC.

2.2 Characterization

The specific surface area (BET) of magnetite and photocatalyst was measured through nitrogen adsorption in a FlowSorb II Micromeritics single point equipment. After ageing time, a portion of TiO_2 was centrifuged in order to analyze its crystalline structure by Raman in GX Perkin Elmer spectrometer. The surface morphology of wet beads and magnetic catalyst was observed by scanning electron microscopy using JEOL model JSM 6480 LV microscopy.

2.3 Photocatalytic test

Photocatalytic activity of the sample was evaluated in a batch photoreactor which consisted of a glass beaker (500 mL) under mechanical stirring with vertical irradiation. The lamp used was a polychromatic Osram Ultra Vitalux 300W lamp with maximum emissions in UV-Visible spectrum zone, as it shows in Figure 1.

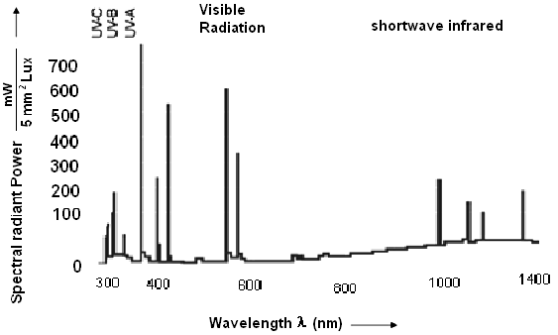

Figure 1: Emission spectrum of the lamp used in the photocatalytic tests.

The evolution of tartrazine degradation was followed by UV-V absorbance on GBC 918 spectrophotometer, equipped with 50W halogen-tungsten and 30W deuterium lamps, at the wavelength of the maximum absorbance of dye, $\lambda = 427.25\ cm^{-1}$.

Firstly, a test was performed without irradiation (light blank) in order to evaluate the adsorption of dye on MC surface. Another test was achieved to analyse the effect of radiation UV on tartrazine decomposition without photocatalyst (TiO_2 blank). Both tests were performed at tartrazine concentration of $2x10^{-5}$ M.

The photocatalytic activity was evaluated at two tartrazine concentrations, $1x10^{-5}$ M y $2x10^{-5}$ M. The tests were performed at room temperature with a catalyst loading of 2 g/L and pH=6 for all cases.

After first test, MC was recovered by a high potential magneto (3500 kgauss), washed and dried at oven at 100 °C. Finally, the photocatalyst reusability was evaluated in five subsequent cycle tests at tartrazine concentration of $1x10^{-5}$ M.

3. RESULTS AND DISCUSSION

3.1 Characterization

BET surface area of magnetite and magnetic photocatalyst were listed in Table 1. The Fe_3O_4 presents a low surface area which shows an important increase after deposition of the titania phase.

Table 1: Specific surface area of magnetite and photocatalyst.

SAMPLE	BET (m^2/g)
Commercial Fe_3O_4	8
MC	29

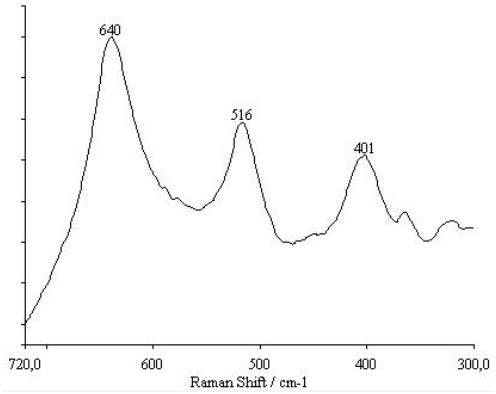

Figure 2: Raman spectrum TiO2 phase obtained before deposition on the magnetic beads.

The Raman spectrum of TiO2 phase is presented in Figure 2. There are three strong absorption bands at 639, 516 and 398 cm-1 which are attributed to Eg, A1g-B1g, and B1g anatase modes, respectively [30]. This confirmed that TiO2 deposited on magnetic cores presented the desirable crystalline phase.

Figure 3 (a) presents a micrograph of a magnetic bead obtained by supercritical drying to avoid the collapse of the internal structure and its interior conformation. Beads present a rough surface as can be seen in the magnifications of the zones 1 and 2 also presented in figure 3 (a). Figure 3 (b) allows to see that the magnetite particles are completely coated by an alginate layer. Figure 3 (c) allows to see that magnetic beads obtained present a homogeneous particle size distribution.

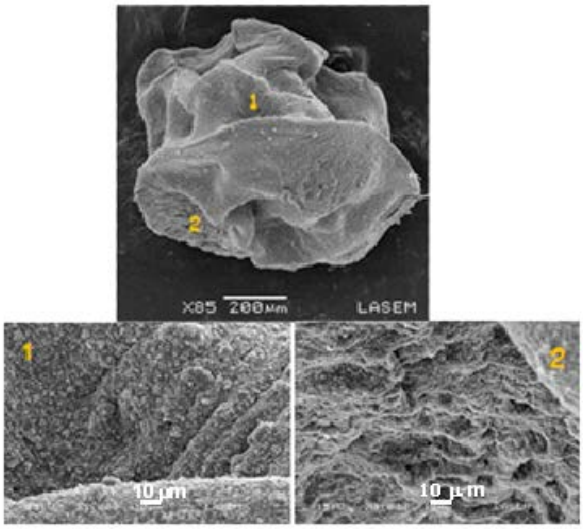

Figure 3(a): SEM micrographs of a magnetic bead, with magnifications in regions 1 and 2.

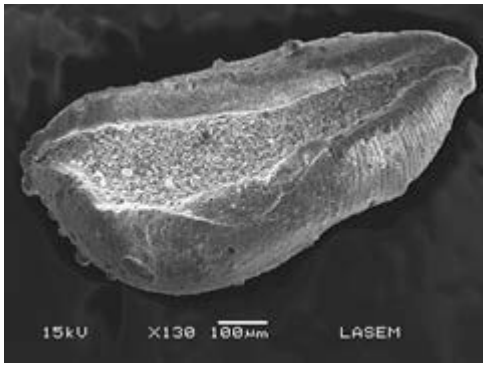

Figure 3 (b): SEM micrograph of a cross-section of a magnetic bead.

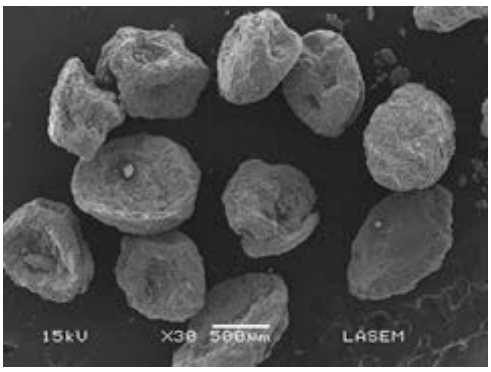

Figure 3 (c): SEM micrograph of magnetic beads showing a homogeneous particle size distribution.

3.2 Photocatalytic activity

In figure 4 is presented the profile of photocatalytic tests at two mentioned tartrazine concentration and adsorption (A) and blank of TiO_2 (B) tests. The percentage of tartrazine degradation was calculated as:

$$\%\deg = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t are the initial and final concentration of tatrazine, respectively.

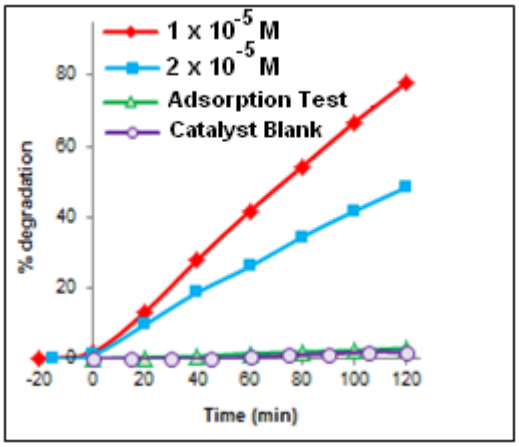

Figure 4: Evolution of Tartrazine degradation with the time of reaction.

In first place, the reduction of tartrazine concentration after adsorption test (light blank) on MC surface, presents a low value after 120 min in contact (3%). The blank of TiO_2 test showed a decomposition of 2% after 120 min of irradiation, due to photolysis process of tartrazine when its molecules are exposed to UV radiation. Both values are very low and its effects can be neglected. In subsequent assays, the solutions with MC were stirring for 20 min before irradiation in order to allow adsorption equilibrium of the dye on catalyst surface.

It can be seen, the photocatalyst MC shows very good photocatalytic activity reaching a rate of tartrazine degradation of around 80%, in 120 min of reaction, for lower dye concentration ($1x10^{-5}$ M). When dye concentration is doubled ($2x10^{-5}$ M), the efficiency of photocatalyst exhibits an important diminution reaching a 48% of decomposition in the same reaction time (120 min). Gupta and co-workers have found similar results for tartrazine degradation using commercial TiO_2 (Aldrich), and they demonstrated the most efficient degradation for an initial concentration of $2x10^{-5}$ M, the lowest concentration used in their work.

3.3 Reusability tests

In Figure 5 is presented reusability tests of magnetic catalyst in five cycles of use. These tests were performed using the optimal tartrazine concentration found it previously, $1x10^{-5}$ M.

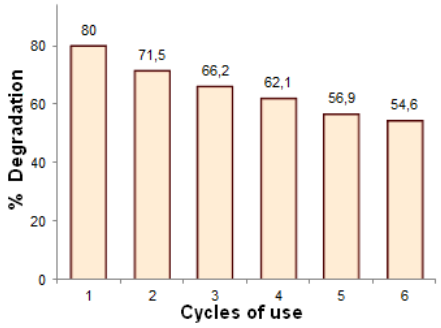

Figure 5: Re-usability cycles tests, the % degradation corresponding to 120 min of reaction.

It can be seen, in the first reuse, MC produces a decrement around 9% in the efficiency of tartrazine degradation, respect for first use. In successive uses, this reduction is lower with an average around 5%, although MC reaches a degradation of dye superior at 50% after six uses. Decreasing between the first and second use can be associated to a possible loss of the anatase layer, probably weakly supported on magnetic beads. Another possibility can be attributed to rests of tartrazine molecules broken down and retained on MC surface.

Results reported in the literature shows that some products of tartrazine photodegradation in the presence of H_2O_2 are acids like 4-phenolsulfonic, fumaric, formic, maleic, oxalic and malonic beside others [32]. Most of these products are known to be biodegradable under various conditions. Although in our case further studies are necessary to elucidate the mechanism and the products of degradation, we can expect than some of these are formed during tartrazine photodegradation with TiO2. All these acids could be adsorbed on anatase and longer contact times are necessary to reach complete mineralization [33].

4. CONCLUSIONS

The magnetic photocatalyst obtained by deposition of anatase TiO_2 on magnetic beads showed a good photoactivity for decomposition of tartrazina dye. Photocatalytic assays were performed for two concentrations of dye showing the best response to degrade tartrazina at $1x10^{-5}$ M. Magnetic properties facilitated its recovery and reusability for five posterior cycles of use, showing a good behaviour yet.

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