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Degradation of AMARANTH with TiO_2 Synthesised by Sol-Gel Process

Degradación de AMARANTH con TiO_2 Sintetizada Mediante Proceso Sol-Gel

MONCADA-SÁNCHEZ, Cristina†, SALAZAR-HERNÁNDEZ, Mercedes*, BALTAZAR-VERA, Juan Carlos and CAUDILLO-GONZÁLEZ, Martín

Universidad de Guanajuato, Departamento de Ingeniería en Minas, Metalurgia y Geología

ID 1st Author: *Cristina, Moncada-Sánchez* / **ORC ID**: 0000-0003-4569-7596

ID 1st Co-author: *Mercedes, Salazar-Hernández* / **ORC ID**: 0000-0001-8039-8124

ID 2nd Co-author: *Juan Carlos Baltazar-Vera* / **ORC ID**: 0000-0056-59510-8300

ID 3rd Co-author: *Martín, Caudillo-González*

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Abstract

The photo-degradation of persistent contaminants in aqueous systems such as drugs, pesticides or dyes has been proposed as an alternative for the remediation of aqueous systems. TiO_2 is one of the main photocatalysts that have been used for these purposes, it has two phases with photocatalytic properties, anatase and rutile, the latter being the one with the lowest conduction band 3.0 eV. The present work shows the synthesis of TiO_2 by sol gel process, observing that the rutile phase is favored with heat treatment at temperatures above 600ºC, the comparative study of the degradation kinetics of AMARANTH with synthesized TiO_2 and commercial TiO_2 was evaluated, observing a rate constant of 1.38 and 0.345 $Lmol^{-1}min^{-1}$ for commercial and synthetic TiO_2, respectively.

Photo-degradation, TiO_2, AMARANTH

Resumen

La foto-degradación de contaminantes persistentes en sistemas acuosos tales como fármacos, pesticidas o colorantes se ha planteado como una alternativa para la remediación de sistemas acuosos. La TiO_2 es uno de los principales foto-catalizadores que se han empleado para estos propósitos, esta presenta dos fases con propiedades fotocatalíticas, anatasa y rutilo, siendo esta última la que presenta la menor banda de conducción 3.0 eV. El presente trabajo muestra la síntesis de TiO_2 mediante proceso sol gel, observándose que la fase de rutilo se favorece con el tratamiento térmico a temperaturas superiores a los 600ºC, se evaluó el estudio comparativo de la cinética de degradación del colorante AMARANTH con la TiO_2 sintetizada y la TiO_2 comercial tratadas a 600ºC, mostraron una constante de velocidad de 1.38 y 0.345 $Lmol^{-1}min^{-1}$ para la TiO_2 comercial y la sintética respectivamente.

Foto-degradación, TiO_2, AMARANTH

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* Correspondence to Author (email: merce@ugto.mx)
† Researcher contributing as first author

Introducción

Nowadays, nanotechnology has taken an important role in the development of new materials, the synthesis of nano-particles has increased in the last decades since at this scale the materials enhance their properties such as hardness, elasticity, thermal conductivity among others, which favours their diverse applications [1-4].

The use of nanoparticles in various areas of technology is very broad, an example of this is the production of a number of TiO_2-based materials, functionalised TiO_2 and TiO_2-Ag, TiO_2-Zn, TiO_2-SiO_2 composites, which have been used as photo-degraders of pollutants in wastewater treatment [1-12]. The interest in the study of TiO_2 particles lies in the fact that its photocatalytic properties make it so useful in fields such as microbiology, medicine, environmental and materials science.

TiO_2, a semiconductor material that absorbs electromagnetic radiation mainly in the Uv region, tends to be thermally and chemically stable, as well as having photocatalytic properties as mentioned above; it is considered a non-toxic oxide, is corrosion resistant and bio-compatible [1-13-15]. It is currently used as a white pigment for paints, as it scatters light more efficiently and is more stable and durable than classical pigments. TiO_2 coatings have high photoactivity and are used in the water and air purification industry by photocatalysis. [12]

Today's increasing pollution has led to the development of new possibilities for remediation procedures. Heterogeneous photocatalysis has been an environmentally friendly method, as it has been shown to degrade organic pollutants at low and medium concentrations [2-10, 17], both in the liquid and gas phase. One of the main materials used in these processes is TiO_2. [16]. In general, this method consists of the degradation of the pollutant through the use of catalysts such as semiconductor oxides (TiO_2, ZnO, among others), ultraviolet and/or solar radiation, generating radicals (O_2·, HO_2·, OH·), which cause the oxidation of the pollutants [17].

Therefore, it has the characteristic of having a particulate photocatalyst suspended in a solution or it can be in contact with a substrate that is in the gas phase, it is irradiated with sufficient energy for photo-excitation to occur. It has been reported that, in order to exploit the visible spectrum, methodologies for material modification, such as the addition of dopant species, have been developed. [15]

The photocatalytic and photodegradation activity of TiO_2 has been enhanced by doping or forming composites with TiO_2 and various additives such as Fe3O4, graphene, silica, Ag, Ru, N, C, Fe, Mo, V, Co and Cu. [3-11]. It is well known that the mechanism by which photo-degradation is generated with semiconductors such as TiO_2, occurs when they adsorb a photon with greater or equal energy than the bandgap energy, an electron from the valence band moves to the conduction band, then the electron and positive hole that was generated migrate to the surface of the catalyst where they participate in oxide-reductive reactions with the absorbed species (pollutant) leading to their degradation and sometimes to their complete mineralisation. [18]

The present work shows the study of the photo-degradation of the AMARATH dye with synthetic TiO_2 obtained by sol-gel process.

Methodology

All the reagents used were reagent grade from Sigma-Aldrich and no purification process was carried out for their use in the syntheses developed.

Synthesis of TiO_2

In a 250 mL ball flask, adapted with a cooler (Figure 1), 70 mL of butanol and 10 mL of titanium terbutoxide were placed, maintaining the temperature at 80°C for 30 minutes, 1 mL of concentrated nitric acid was added to the solution and kept under constant agitation for 5 minutes to homogenise the solution. Slowly add 5 mL of deionised water over a period of 15 minutes until gel formation is observed in the system. Once the gel is obtained, the system is kept under reflux for 30 minutes. The obtained gel is recovered and dried at 70ºC for 12 h. The solid obtained is subjected to heat treatment for 1 and 2 h at 500, 550, 600, 650 and 700 ºC.

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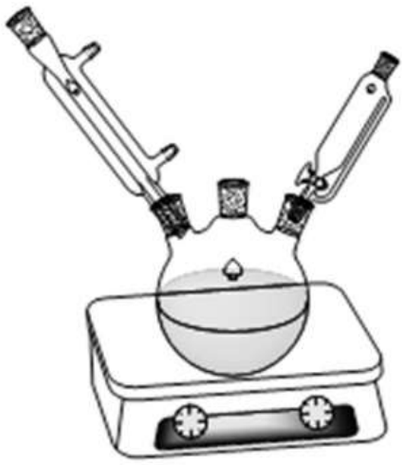

Figure 1 Reaction system for the production of TiO_2

Characterisation

The characterisation of TiO_2-c and TiO_2-s was performed by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Morphology was evaluated using a Joel-6510 plus microscope and XRD was obtained on a RIGAKU ULTIMA IV diffractogram.

AMARANTH® Dye Photo-Degradation Studies

The photo-catalytic degradation tests of the dye were evaluated by degradation kinetics, against commercial TiO_2 (TiO_2-c) and synthesised TiO_2 (TiO_2-s). 0.2 g of the material to be evaluated (TiO_2-c and TiO_2-s) is added with 20 mL of a 3.52X10-3M Amaranth dye solution. The residual concentration of the dye in the solution is evaluated every 20 min by Uv-visible spectroscopy at 520 nm.

Results

The XRD characterisation of commercial and synthesised TiO_2 showed the presence of the anatase phase, which is the phase with the highest conduction band (3.2 eV) (Figure 2), the rutile phase presents a conduction band of 3. 0 eV, lower than that of the anatase phase, which is why this phase is preferable for photocatalytic applications in the degradation of pollutants; for this reason, the effect of heat treatment at 500, 550, 600, 650 and 700 ºC on the synthesis of the material was evaluated. The formation of the rutile phase was observed from 550ºC onwards, favouring it from 600 ºC, where a composition of 70% of the rutile phase was observed in the material (Figure 3).

At 700 ºC a composition of 80% of the rutile phase was observed, so it could be considered a quantitative composition of the rutile phase with thermal treatments above 700ºC, however at these high temperatures the sintering process of the materials is observed, which considerably reduces the surface area of these, disfavouring the contact area of the material with the analytes to adsorb or degrade in a photo-degradation process, that is why the temperature at 600-650ºC was considered as the most suitable for the synthesis of the material.

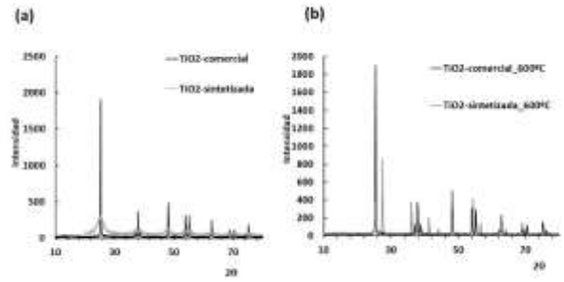

Figure 2 XRD TiO_2-c and TiO_2-s

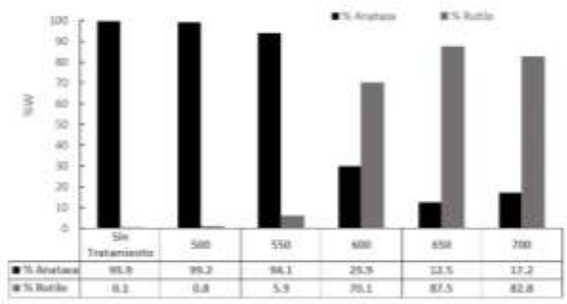

Figure 3 Effect of temperature on the formation of rutile phase

Figure 4 shows the characterisation of the material by SEM, where the presence of condensed particles is observed, as well as no change in the texture and morphology of the material with the thermal treatment (Figure 4b).

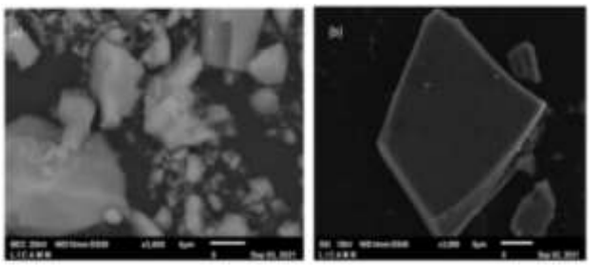

Figure 4 SEM characterisation of TiO_2 synthesised (a) without heat treatment and (b) treated at 600°C

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AMARANTH Dye Photo-Degradation Studies

The degradation of the AMARANTH dye with synthetic and commercial TiO_2 was evaluated by following the concentration of the dye with respect to time once in contact with the material and UV light. It should be mentioned that both materials (TiO_2-c and TiO_2-s) were placed in contact with the dye without UV radiation, showing a decrease in the dye concentration by 2.5 %, in an initial period of 20 minutes of contact, this is due to the adsorption of the dye on the materials and not to photo-degradation.

Figure 5 shows the degradation kinetics of AMARANTH, where it can be observed that TiO_2-c shows a higher degradation of the dye by 37%, reaching equilibrium after 140min, while TiO_2-s only reached 22% degradation, however the equilibrium of the system is not observed, so the degradation kinetics that this material offers is slower. The experimental data were adjusted to the second order model, observing rate constants of 1.39 Lmol-1min-1 and 0.345 Lmol-1min-1, being 4 times higher the degradation rate offered by TiO_2-c than the one observed with TiO_2-s. This difference could be due to the textural properties of the materials, considering that TiO_2-s could have a lower surface area than TiO_2-c due to the sintering of the surface caused by the heat treatment temperature.

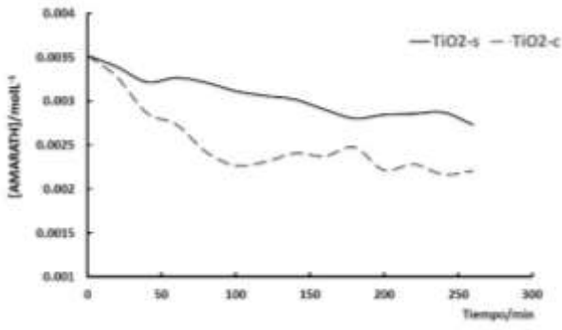

Figure 5 Photo-degradation kinetics of the dye AMARANTH

Conclusions

The formation of the rutile phase, which is the crystalline phase with the lowest conduction band, is favoured by treatments at 600ºC.

The comparative study of the photocatalytic degradation kinetics of the AMARANTH dye TiO_2-c and TiO_2-s showed the degradation of 37 and 22% of the dye with TiO_2-c and TiO_2-s respectively, with TiO_2-c reaching equilibrium at 140 min of exposure. The experimental data were fitted to the second-order model, observing rate constants of 1.39 Lmol-1min-1 and 0.345 Lmol-1min-1, with the degradation rate offered by TiO_2-c being 4 times higher than that observed with TiO_2-s.

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