Enhanced of TiO_2-Ag photocatalysis performance for removal of methylene blue in the presence of acetone

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Abstract
In the present study, the photocatalytic degradation of methylene blue (MB), using TiO_2-Ag synthesized by sol-gel method, as a catalyst under UV light, was studied. Tests were carried out in a batch reactor, magnetically stirred, with external irradiation using an UV-B. The effects of some parameters, such as catalyst dosage and initial acetone concentration were investigated. Results showed that the optimal catalyst concentration was 0.03 g/L, at a concentration of MB of $1.25 \cdot 10^{-5}$ mol/L. The results are very promising using TiO_2-Ag as photocatalyst, especially in the presence of acetone as photosensitizer; the degradation degree increases from 60% for raw TiO_2, to 92.38% for TiO_2-Ag and 0.1% acetone and respectively, 97.25% for 0.2% acetone. The photocatalysis followed a pseudo-first order reaction kinetics, with rate constants ranging from 0.0009 to 0.11 min^{-1} under the studied conditions.
Keywords: TiO_2-Ag, photocatalytic degradation, Methylene blue, acetone, kinetics

1. Introduction

The over 100,000 different types of dyes, with 7.10^5 tones/years are produced, from which 10% are lost during the dyeing process and discarded in water effluents. The dyes from wastewater cause considerable environmental pollution and serious health risk. The methods developed for the removal of dyes from wastewaters are the solvent extraction, the adsorption and chemical treatments process. However, often these procedures issue by-products and solid wastes. Remarkably, the photocatalytic degradation solves water cleaning (Sangpour et al., 2010) without producing extra waste.

Titanium dioxide is extensively used for the pollutants removal from wastewater because of its stability, high photocatalytic activity, low-toxicity, low cost etc. The advantage of TiO_2 as photocatalyst is that the dyes are usually completely mineralized. The photocatalytic activity of TiO_2 can be enhanced by several methods: doping, surface modification, shape tailoring. Among the noble metals (Me), Pt, Ag, Au, Pd, Mo and Ru have been widely investigated and have been reported to favor the photocatalytic reactions yields. Silver is particularly attractive, due to its remarkable catalytic activity, on one part, and due to its possible applications in biological and chemical applications and its antibacterial properties, on another part.

TiO_2 with Ag nanoparticles can be relatively easily obtained through the sol-gel method, a versatile method for this purpose. TiO_2-Ag nanocomposites with increased homogeneity can be obtained by the sol-gel method and the particle size can be easily controlled (Nuțescu Duduman et al., 2018). The photodegradation of dyes is enhancing by using acetone as photosensitizer.

The objective of this study is to evaluate the performance of the photocatalytic process in the elimination of methylene blue (MB) from aqueous solutions, under UV irradiation. The influence of the acetone concentration was studied and the photodegradation reaction kinetics were discussed. The kinetic constants were determined for all synthesized materials.

2. Materials and Methods

The reagents used for the synthesis were: titanium isopropoxide ($C_{12}H_{28}O_4Ti$), silver nitrate ($AgNO_3$), hydrazine (N_2H_4), ethanol (C_2H_6O), nitric acid (HNO_3) 65% (as a hydrolyzing agent) and ammonia – 0.1M (as a neutralizer). The samples were labeled as: pure TiO_2 (S1), TiO_2-Ag (S2) and TiO_2 – Ag calcined for 2 h at 650°C (S3) (Gómez de Castro et al., 2017). The irradiation source was an UV-B lamp of Hg - 18 W, with incident radiation intensity of 2.1 W/m^2. Experiments were performed in a 100 mL volume reactor, at 25°C. 50 mL of 14 ppm MB solution was placed into the reactor and stirred for 20 min in the dark. The MB concentration was measured by spectrophotometry, based on the main peak at 664 nm. The reactions were performed at the native pH of the dye solution of 6.5. At due time intervals, slurry samples from the photoreactor were taken, separated by centrifugation, then absorbance was read; three parallel readings were made. The egradation yield of

the MB solution was calculated according to the equation:

$$R\ (\%) = 100\ (C_0-C_t)/C_0 = 100\ (A_0-A_t)/A_0,\ \%\qquad (1)$$

where R (%) was the dye degradation extent, C_0 and C_t were the concentrations of MB initially and at time t; A_0 and A_t were the absorbance values of MB dyes solution initially and at and time t.

3. Result and Discussion

The experimental data proved that during the direct photolysis (UV action only, no photocatalyst), only 2% of the initial dye concentration was degraded. In the presence of samples S1 and S2, some of the dye was decolorized and the silver nanoparticles slightly improved the photodegradation. The use of acetone as photosensitizer improved in a spectacular extent the MB decolorization. (Fig. 1). The beneficial effect is a lot better on the samples containing silver. At 0.1% acetone, the degradation yield increases at 88.12% on S2, respectively 92.38% on S3. When increasing the acetone concentration to 0.2%, the photodegradation reached about 98% on all three samples. The enhancement of the photocatalytic performance of the Ag-TiO2 samples S2 and S3 might be attributed to narrowing of the band gap. .

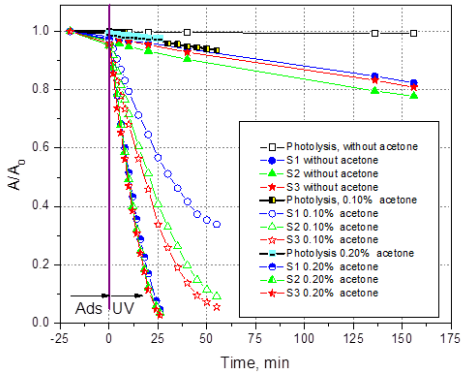

Figure 1. Photodegradation of MB using S1-S3 photocatalysts

The effect of the dose of catalyst on the MB degradation was studied at four values, 0.01, 0.02, 0.03 and 0.04 g catalyst/L, at an initial 4 ppm dye solution, running 60 min. The degradation grade increases with the catalysis dose, reaching an optimum at 0.03g/L. All the dye molecules are probably adsorbed on TiO_2 in these conditions and the addition of higher amounts of TiO_2 have no extra-effect on the degradation process. The photocatalysis followed a pseudo-first order reaction kinetic behavior, with rate constants ranging from 0.0009 to 0.0012 min^{-1}. The pseudo-first order rate constant values were 0.02 and 0.1 min^{-1} under UV light irradiation.

4. Conclusions

In this study, TiO_2-Ag nanocomposites with superior catalytic performance has been synthesized by a facile sol–gel method. A comparison was made between a sample just impregnated with silver nitrate and a calcined one at 600°C. The TiO_2-based materials displayed a quite low activity in the photodegradation of MB alone. When very small amounts of acetone were used as a photosensitizer, the efficiency for the degradation of MB increased in a spectacular extent even at low doses as 0.1%. At a sensitizer concentration of 0.2%, the photocatalytic degradation was almost complete after only 25 minutes.

The role of the photocatalyst dose highlighted an optimum value of 0.03 g/L.

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