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Synthesis of boron and silver co-doped TiO_2 photocatalysts for the degradation of the antibiotic Sulfamethoxazole in aqueous solutions

KARAFINA P.[1], TYROVOLA K.[1], DROSOU C.[1], AND XEKOUKOULOTAKIS N. P. [1,*].

[1]School of Environmental Engineering, Technical University of Crete, University Campus, GR-73100 Chania, Greece

*corresponding author: Xekoukoulotakis, N.P.
e-mail: nikos.xekoukoulotaki@enveng.tuc.gr

Abstract. The present work studied the preparation of various boron and silver co-doped photocatalysts, using titanium isopropoxide as a starting material, and the comparison of their efficiency with the commercial TiO_2 catalyst Degussa P25. The doped photocatalysts were prepared by the solvothermal method. Photocatalysis experiments were carried out under both solar irradiation and visible light to evaluate the influence of doped and undoped TiO_2 catalysts on the degradation of the antibiotic sulfamethoxazole (SMX). According to the results, boron doped photocatalysts contributed the most to SMX removal from aquatic solutions, although the most efficient catalyst of all proved to be titanium dioxide (TiO_2).

Keywords: photocatalysis, solar, visible, doping, SMX

1. Introduction

Pharmaceuticals have been detected in a wide variety of environmental matrices over the past few years. Most of the pharmaceuticals are partly degraded in the waste water treatment plants (WWTPs) and they are discharged in aquatic environments. The presence of antibiotics in aqueous compartments of the environment is considered to be a severe emerging issue due to the potential risks for aquatic organisms and humans (Homem and Santos, 2011).

Sulfamethoxazole (SMX) is an antibiotic which is worldwide used to treat infections caused by bacteria. SMX is composed of sulfanilamide and isoxazole. This structure acts as a deterrent to bacterial growth (Chamberlain and Adams, 2006). Advanced oxidation processes (AOPs) consists of a wide series of innovative processes that are environmentally friendly. Their application in WWTPs has shown successful results in the removal of pharmaceuticals and other harmful and toxic substances (Parsons, 2004). This study aimed to examine the efficiency of various doped TiO_2 photocatalysts in SMX degradation.

2. Materials and methods

2.1. Synthethis of photocatalysts

The solvothermal method was adopted for the preparation of various boron and silver co-doped TiO_2 photocatalysts (Feng et al., 2013). B-doped (with molar ratios of B/Ti=0.005, 0.02, 0.05, 0.10 and 0.20), Ag-doped (with molar ratios of Ag/Ti=0.005, 0.01, 0.03 and 0.05), (B, Ag)-co-doped (with molar ratios of B/Ag/Ti=0.10-0.005, 0.10-0.01, 0.10-0.03 and 0.10-0.05) and pure TiO_2 catalysts were prepared in specific amounts of boric acid, silver nitrate and titanium isopropoxide (TIP). A mixture of 180 mL ethanol/water was the medium in which boric acid and silver nitrate were dissolved. This solution mixture was continuously stirring, and 0.033 mol of titanium isopropoxide was added dropwise. The resultant mixture was left for 12 h under stirring at room temperature. Subsequently, it was transferred for further hydrothermal treatment at 358 K for 250 min in a Teflon bottle. After cooled to room temperature, the catalysts were separated by centrifugation, washed several times with ultra pure water, and dried at 373 K. Calcination treatment in air at 673 K for 4 hours was conducted to obtain the final catalysts.

2.2. Sulfamethoxazole photocatalysis

Photocatalytic experiments were performed in two laboratory scale reactors. The first reactor was a solar radiation simulator (Newport, model 96000) equipped with a 150 W Xenon ozone-free lamp emitting in the solar region of the electromagnetic spectrum and the second reactor consisted of 4 Cool White Lumilux 18W/840 Osram lamps. The experiments were performed with the use of doped prepared TiO_2 catalysts as the photocatalytic medium. The samples taken were centrifuged for 15 minutes to remove catalyst particles. In addition, TiO_2 photocatalysis and photolysis experiments were conducted. SMX concentration was detected by high performance liquid chromatography (HPLC) equipped with a diode array detector and a C18 Supelco column (5 μm, 4.6 mm×150 mm). The mobile phase was a mixture of phosphate buffer 20 mM (pH ~4.16) and acetonitrile in 60:40 volumetric ratio eluted isocratically with a flow rate of 1 mL/min. The injector volume was 100 μL, and the column temperature was 30 ºC. The detection of SMX was accomplished by the diode array detector set at 269 nm.

3. Results and discussion

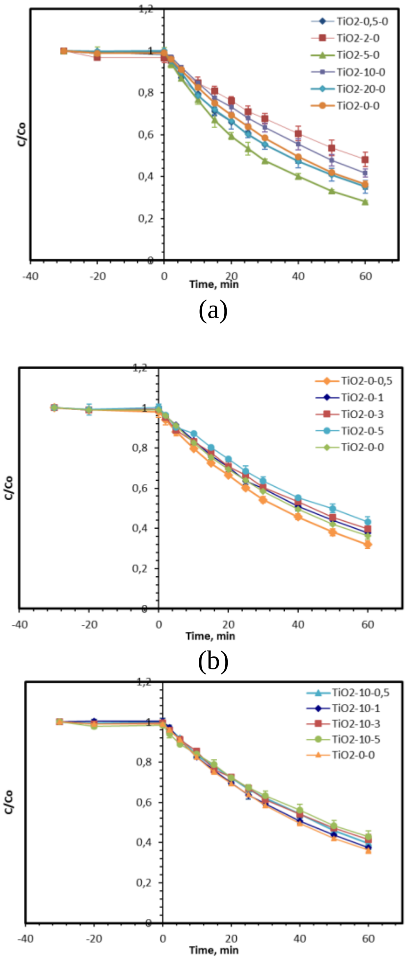
3.1. Doping

B-doped, Ag-doped, (B, Ag)-co-doped and undoped TiO_2 catalysts were prepared in specific amounts of boric acid, silver nitrate, and titanium isopropoxide to investigate their ability to remove SMX from aqueous matrices. The synthesized photocatalysts are designated as TiO_2-x-y, where x and y is the mol ratio of boron and silver, respectively. The stabilization of the pH value between 6.5 to 7.5 signalled the end of the washing process and the samples were dried in the oven. The process of washing aimed at the removal of contaminants and initial products and the achievement of a pH value, as close as possible to 7, because this value is related to the isoelectric point of titanium dioxide, which is between 5.8-7.5 (Beranek, 2011).

3.2. Sulfamethoxazole degradation

The photocatalytic degradation of SMX was performed with the use of the commercially available catalyst Degussa P25 and the catalysts prepared by the hydrothermal method. The activity of the photocatalysts was investigated under simulated solar radiation and visible light.

Solar photocatalysis experiments showed that the increase of boric acid amount above a certain degree in the mole proportion preparation of the catalysts operated negatively in the improvement of the photocatalyst activity. The most efficient catalyst proved to be the one with 5% boron, achieving removal of 70% of the initial concentration of the SMX in 60 minutes. The use of Ag-doped catalysts showed that as the added amount of silver nitrate was increased, the photocatalytic effect of SMX removal was decreased. Figure 1 proves that the Ag-doped catalyst which contributed the most to the degradation of SMX was the 0.5% Ag-doped, resulting in the 65% removal of the initial concentration of SMX. In contrast, the less efficient catalyst appeared the one with the greatest amount of silver (5%), which removed the substance by approximately 50% for the same period of time. The catalyst that showed the best performance for SMX removal was the one doped with 10% boron and 1% silver. However, even better results seem to have the catalyst prepared by the precursor of TiO_2, without being enhanced by boron or silver. The activity of the particular catalyst can be justified by impurities that may have been created during the preparation process, which could be proven by further experimental analysis and measurements.



(a)

(b)

(c)

Figure 1. Photocatalytic degradation of SMX under simulated solar radiation using: (a) B-doped photocatalysts; (b) Ag-doped photocatalysts; and (c) B-Ag-codoped photocatalysts.

The photocatalytic reactions rate can be calculated according to the following equation: $r = \frac{dC}{dt} = k \times C$

where r is the reaction rate (in mol·L^{-1}·min^{-1}), k is the pseudo first order rate constant of SMX oxidation (in min^{-1}) and C is the concentration of SMX (in mol·L^{-1}).

The reaction rate constants were determined from the slope of the line resulting from the graph of $-\ln(C_t/C_0)$

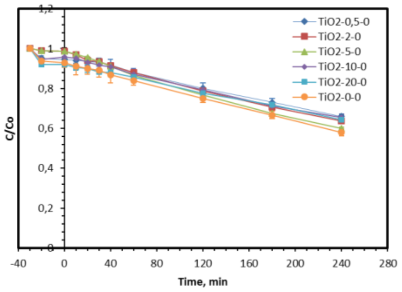
versus time, using linear regression. The calculated constants for each catalyst used in solar photocatalytic experiments are given in Table 1. As shown, the catalyst with 5% boron is the fastest for the decomposition of SMX with k = 1.80×10^{-2} min^{-1}. Among the Ag-doped catalysts the fastest in photocatalytic decomposition of the substance under simulated solar radiation turns out to be the catalyst with 0.5% Ag, with the constant k equal to 1.90×10^{-2} min^{-1}. This fact confirms that the increase of silver nitrate in the mole ratio preparation leads to the reduction of the sulfamethoxazole decomposition rate. As far as the B-Ag-co-doped catalysts are concerned, their efficiency did not vary significantly. In addition, prestine TiO_2-0-0 catalyst showed quite high photocatalytic activity with k = 1.72×10^{-2} min^{-1}. The very high values of the coefficient of determination demonstrate the very good fitting of the experimental data to the first order equation.

In addition, the efficiency of the photocatalysts was examined under visible light. Photocatalytic experiments were conducted in a laboratory scale reactor with lamps emitting in the visible region of the electromagnetic spectrum. In aqueous solution with initial SMX concentration of 2.5 mg·L^{-1} was added 250 mg·L^{-1} of each catalyst. The mixture was left for 10 minutes in an ultrasonic device to achieve the dispersion of the catalyst and the equal distribution of the solution. Photocatalytic experiments under visible light lasted for 240 min each. It was found that the synthesized catalyst TiO_2-5-0 resulted in 40% removal of SMX. In contrast, the less efficient catalyst proved to be TiO_2-20-0, achieving only 20% removal of SMX for the same period of time. Ag-doped photocatalysts showed similar results under visible light for all proportions of silver doping. Co-doping was more effective for low amounts of B and Ag doping. TiO2-0.5-1 was the most efficient co-doped catalyst. The increase of the silver amount in combination with the constant amount of boron did not improve the photocatalytic activity.

TiO_2 photocatalysis experiments under solar and visible light were conducted to compare the results with the doped photocatalysts. The TiO_2 activity under simulated solar radiation achieved total removal of SMX at the first 60 minutes of the photocatalytic process. TiO_2 photocatalysis under visible light led to 80% SMX decomposition in four hours, although this was not expected due to the inability of titanium dioxide to be activated in the visible region of the electromagnetic spectrum. This fact can be justified by the emission spectra of the used lamps as a visible light radiation source. In fact, the existence of spectral emission lines observed in the range of 300 to 400 nm was enough to activate Degussa P25. Degussa P25 succeeded much faster removal rates of SMX with constant k equal to 4.99×10^{-2} min^{-1} under solar radiation and 7.3×10^{-3} min^{-1} under visible light. The superiority of Degussa over all other prepared photocatalysts may be attributed to surface slow recombination of electrons and holes (e^-/h^+), and the structure mixture of anatase and rutile, which makes the catalyst activity greater than that of pure crystalline forms (Abellan et al., 2009).

Table 1. Kinetic rate constants of doped catalysts for SMX photocatalytic degradation under simulated solar radiation

Catalyst	**Mol proportion**	**k (min^{-1})**
TiO_2–0–0	TIP-0%B-0%Ag	1.72×10^{-2}
TiO_2–0.5–0	TIP-0.5%B-0%Ag	1.80×10^{-2}
TiO_2–2–0	TIP-2%B-0%Ag	1.18×10^{-2}
TiO_2–5–0	TIP-5%B-0%Ag	2.25×10^{-2}
TiO_2–10-0	TIP-10%B-0%Ag	1.48×10^{-2}
TiO_2–20–0	TIP-20%B-0%Ag	1.85×10^{-2}
TiO_2–0– 0.5	TIP-0%B-0.5%Ag	1.90×10^{-2}
TiO_2–0–1	TIP-0%B-1%Ag	1.65×10^{-2}
TiO_2–0–3	TIP-0%B-3%Ag	1.57×10^{-2}
TiO_2–0–5	TIP-0%B-5%Ag	1.43×10^{-2}
TiO_2–10–0.5	TIP-10%B-0.5%Ag	1.56×10^{-2}
TiO_2–10–1	TIP-10%B-1%Ag	1.69×10^{-2}
TiO_2–10–3	TIP-10%B-3%Ag	1.51×10^{-2}
TiO_2–10–5	TIP-10%B-5%Ag	1.42×10^{-2}



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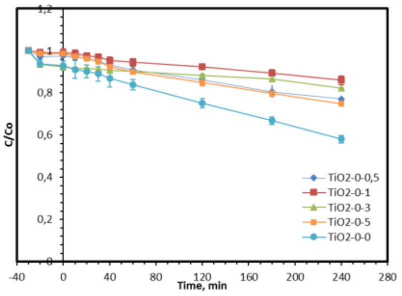

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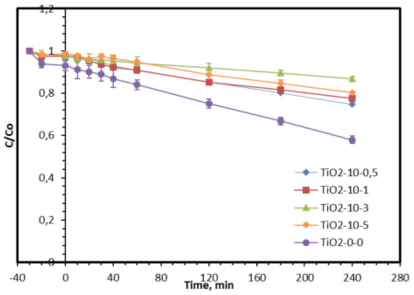

(c)

Figure 2. Photocatalytic degradation of SMX under visible light using: (a) B-doped photocatalysts; (b) Ag-doped photocatalysts; and (c) B-Ag-codoped photocatalysts.

Table 2. Kinetic constants of doped catalysts for SMX photocatalytic degradation under the effect of visible light

Catalyst	Mol proportion	k (min^{-1})
TiO_2–0–0	TIP-0%B-0%Ag	1.90*10^{-3}
TiO_2–0.5–0	TIP-0.5%B-0%Ag	1.60*10^{-3}
TiO_2–2–0	TIP-2%B-0%Ag	1.80*10^{-3}
TiO_2–5–0	TIP-5%B-0%Ag	2.10*10^{-3}
TiO_2–10-0	TIP-10%B-0%Ag	1.60*10^{-3}
TiO_2–20–0	TIP-20%B-0%Ag	1.40*10^{-3}
TiO_2–0– 0.5	TIP-0%B-0.5%Ag	1.00*10^{-3}
TiO_2–0–1	TIP-0%B-1%Ag	6.00*10^{-3}
TiO_2–0–3	TIP-0%B-3%Ag	4.00*10^{-3}
TiO_2–0–5	TIP-0%B-5%Ag	1.20*10^{-3}
TiO_2–10–0.5	TIP-10%B-0.5%Ag	1.10*10^{-3}
TiO_2–10–1	TIP-10%B-1%Ag	1.00*10^{-3}
TiO_2–10–3	TIP-10%B-3%Ag	5.00*10^{-3}
TiO_2–10–5	TIP-10%B-5%Ag	8.00*10^{-3}

4. Conclusions

SMX is a very stable pharmaceutical substance. The doped photocatalysts, prepared with the solvothermal method, exhibited significant photocatalytic activity under simulated solar radiation. Among them, the catalyst doped with 5% B, proved to be the most effective, contributing to the SMX degradation by approximately 70% in 60 minutes. Photocatalytic activity of enhanced catalysts also appeared in the visible region of the electromagnetic spectrum, but to a quite less extent. Compared to all used photocatalysts, the commercially available catalyst, Degussa P25, showed greater effectiveness in the degradation of SMX, achieving the complete removal of the substance under solar radiation in 60 minutes and 80% degradation under visible radiation over 4 hours.

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