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Photocatalytic Destruction of Amoxicillin in a Pilot Sunlight Reactor With Supported Titania Nano-Photocatalyst

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Pharmaceuticals and Personal Care Products (PPCPs) are the emerging pollutants threatening the aquatic life even at low concentration due to their chronic discharges into surface streams. During last decades, titania photocatalysis opened a promising method for Amoxicillin (AMX) abatement in aqueous solution. However, using a photocatalytic powder creates by itself a source of a new pollution. We report on the use of the supported titania nano-photocatalyst in a pilot solar reactor for AMX removal in aqueous solutions. Titanium oxo-alkoxy nanoparticles were prepared in a sol-gel micromixing reactor and coated on a 5-mm diameter borosilicate glass beads. Further heat treatment resulted in anatase coatings of 8 nm thickness. About 450 g of the beads were placed in a main tube of a photocatalytic pilot solar reactor of 150 cm length and 5 cm diameter. Aqueous solutions of AMX 10 mg/L in distilled water were prepared and submitted to the solar tests. Thereafter, pH of the solution was adjusted at 3.5, 7.5 and 9.5 using H₂SO₄ and NaOH. The total duration of one run was 240 min and the accumulated UV energy was about 35 kJ_{UV}/L of solution depending on time of day. The obtained results showed that AMX degradation reaches 76% after 240 min exposure for pH 9.5 and 60% for pH 7.5. The photocatalytic reactor yield remained unchanged after 6 cycles of 240 min treatment; no appreciable deactivation and/or degradation of the nano-photocatalyst were observed. An addition of H₂O₂ did not appreciably affect AMX degradation. A comparison with the commercial TiO₂ powder was carried out in similar experimental conditions and solar exposure in parallel run mode; it showed the higher energetic efficiency of the supported nanocatalyst.

1. Introduction

Water is essential to life on earth and human health. Emerging pollutants including antibiotics have been observed in surface water, ground water, sewage effluent and even in drinking water (Ayodele et al., 2012, Trovó et al., 2008). Among the various pharmaceutical compounds, antibiotics have been paid particular attention because of their potential role in the development of antibiotic-resistant bacteria (Ayodele et al., 2012, Elmolla and Chaudhuri, 2010, Trovó et al., 2008, Dimitrakopoulou et al., 2012). It is well established that western countries are the principal PPCPs consumers with 70% of the market compared with other areas of the Globe. However, due to the high costs the conventional waste water treatment is not commonly employed in Asia and Africa, where PPCPs in rivers reaches high concentrations: e.g. 1.49 ng/L of antibiotics against 0.53 ng/L in western countries. Thus low cost and eco-friendly sustainable alternatives are yet to be developed in order to reduce the environmental pollution. The solar heterogeneous photocatalytic detoxification process consists in utilizing the near-UV part of the solar spectrum to photoexcite a semiconductor catalyst in the presence of oxygen. In these circumstances oxidizing species, either bound hydroxyl radical ([•]OH) or free holes, which attack oxidizable contaminants, are generated producing a progressive breaking of molecules yielding to CO₂, H₂O and dilute inorganic acids (Pereira et al., 2014, Sousa et al., 2013, De la Cruz et al., 2013, Prieto-Rodríguez et al., 2013, Pereira et al., 2013, Prieto-Rodríguez et al., 2012, Alalm et al., 2015).

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There are some works dealing with TiO₂ photocatalytic method for AMX degradation: Pereira et al. investigated the enhancement of the photocatalytic degradation of AMX (20 and 40 mg/L) in a CPC pilot plant. The use of solar photoreactor was shown to be effective for the degradation of the antibiotic AMX in aqueous solution at neutral pH (Pereira et al., 2014).

In another study, TiO₂-patterned PI film catalysts were synthesized. Under UVA irradiation, AMX, ATZ, and 4-CP decreased with increasing photocatalysis time. Results indicate that their oxidation products are less toxic than the parent compounds (Ramasundaram et al., 2017).

In a recent work we presented results of degradation of AMX by using powder TiO₂ (Aldrich) in a solar tubular reactor (Moosavi and Tavakoli, 2016). If many studies have been carried out under UV light however few works demonstrated the photocatalytic degradation of Amoxicillin under natural sunlight in a pilot reactor by TiO₂ fixed on the surface of glass beads. The method using TiO₂ powder has the inconvenient of dispersing TiO₂ in the natural streams leading to a new pollution specifically at nanometric scale and the additional cost of the lost TiO₂. In this paper we'll present the experimental results of degradation of Amoxicillin carried out on nanoparticles of TiO₂ elaborated and fixed on the surface of 5mm glass beads by sol gel method. Addition of zirconium atoms to the lattice of TiO₂ is expected to modify the band gap and therefore the photochemical activity of TiO₂. In a recent work (Cheng, 2018) it has been demonstrated that Ti_(1-x)O_(2+x)Zr_x composites enhances the ethylene abatement in gas phase. Two type of Ti_(1-x)O_(2+x)Zr_x with x = 0 and 0,05 were prepared and the influences on AMX degradation under solar light were compared in this work.

2. Experimental procedure

The preparation of the photocatalysts in a sol gel micromixing reactor was performed following the procedure described in a previous papers (Rivallin et al., 2005, Azouani et al., 2010) resumed below. Two compositions Ti_(1-x)O_(2+x)Zr_x (x = 0 and x = 0.05) were selected to do experiments referring to optimum conditions.

2.1 Synthesis

Titanium oxo-alkoxy nanoparticles were prepared in a sol-gel micromixing reactor (Rivallin et al., 2005, Azouani et al., 2010) and coated on 5 mm diameter borosilicate glass beads. The solutions of precursor and water to synthesize colloidal solution of titanium oxide were prepared in a LABstar glove box workstation (MBraun) for avoiding of any contamination from atmospheric humidity (the vapour of H₂O was kept at below than 0.5 ppm). Two A stock solutions of precursors were prepared: (A) zirconium-tetraisopropoxide (98%, Sigma-Aldrich) and titanium-tetraisopropoxide (98%, Sigma-Aldrich); (B) bi-distilled filtered water in n-propanol (99.5%, Sigma-Aldrich) used as solvent.

The total of titanium precursors concentrations was kept at 0.292 M and hydrolysis ratio according to Cheng et al. (Cheng et al., 2017).

$$H = \frac{C_{H_2O}}{(C_{Zr} + C_{Ti})} = 1.25 \quad (1)$$

These solutions were transferred and injected into the tanks (A) and (B) of the micro-mixing reactor. The nitrogen pressure of 4 bar were used for applying to mix (A) and (B) solutions at T-mixer in order to reach the Reynold's number $Re \approx 6000$. The micro-mixing reactor is made up of the metal tube having the inner diameter of 1 mm for the input arms joining the tanks (A) and (B) to a an output metal tube of 2 mm in diameter. This permits to develop vortex when the two liquids meet together fast and thus leading to produce nano-metric TiO₂ particles. The mixed fluid flow rate was about 10 m/s, which is believed faster than the nucleation and growing phenomena, with control temperature at 20 °C by a thermo-cryostat Haake, DC10K15. The nanoparticles sizes were about 3.2 nm diameter according to previous measuring procedure (Cheng et al., 2017).

The borosilicate glass beads with 5 mm diameter were put and kept in concentrated sulfuric acid (95-98%) overnight and then well cleaned with distilled water until 10 times. Then they were dried in the oven (at 80 °C around overnight). After the obtained colloidal solutions had been mixed by micromixing reactor and transferred into glove box, these dried borosilicate glass beads were coated during 10 min with these nanoparticles. The coated beads were filtered with filter papers and dried at temperature around 70 °C.

The different treatment temperatures were chosen due to different crystalline temperatures of the material and referred to the optimum calcinations for enhanced photocatalytic activity of ethylene photodegradation in gas phase. The film coated pure oxo-TiO₂ on borosilicate beads were treated at 450 °C in 4 hours, but at 500 °C for Zr_{0.05}Ti_{0.95}O₂.

2.2 Photocatalytic Evaluation

The Solar photocatalytic experiments were carried out in a pilot plant with CPCs installed at the solar site in the Chemical Engineering Department of faculty of Engineering, university of Isfahan, Iran. The solar reactor consisted of a CPC unit of 4 borosilicate glass tubes arranged horizontally and connected in series by polypropylene junctions with their reflectors covered by polished aluminium. The bottom of one of the borosilicate tubes was lined with the glass beads (453 g = 3113 pieces) covered with TiO₂ catalyst. Transmissivity of low iron glass tubes and beads is about 90% for irradiations wavelength between 380 nm and 2000 nm.

The pilot plant is fixed and tilted at the local latitude (33°) in order to receive perpendicularly the sunlight.



Figure 1: The Solar reactor CPC unit of 4 borosilicate glass tubes equipped with tanks and pumps for recirculation of AMX solutions.

Amoxicillin AMX (Mw: 365.4) was purchased from ZHUHAI (China). Lots of 10 L distilled water containing 10mg AMX, used as pollutant molecule, were prepared and put in the solar reactor's tanks. The pH of solution was adjusted by H₂SO₄ and NaOH (Merck).

The AMX solution was pumped directly from the tank then passed through the tubes arranged in series and submitted to solar irradiation before returning to the tank. This solution was recycled several times during four hours at a rate of 20 L/min. The accumulated UV energy received on any surface in the same position with regard to the sun calculated by equation:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV_{G,n}} \frac{A_r}{1000 \times V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (2)$$

Where t_n is the experimental time for each sample (s), V_t is the total volume of wastewater at n water sample (L), A_r is illuminated collector surface area (m²), $Q_{UV,n}$ is the accumulated energy (kJ/L), $UV_{G,n}$ is the average solar UV radiation during Δt_n (W/m²).

3. Results

3.1 Characterization

Nano particles of Ti_(1-x)O_(2+x)Zr_x were characterized by XRD (EQUINOX 1000-Inel), TEM (JEOL2011) and ICP (iCAP 6000) and BET (COULTER SA3100). These characterizations were carried out on the coatings when applicable, otherwise they were down on powder solids prepared in the same experimental conditions. The size of the prepared nanoparticles depended on the elemental concentrations in the precursor solutions. The average diameter of obtained crystallites ranged around 3.2 nm for $x = 0$ to $x = 0,05$. However the average diameter enhances to 4.2 nm when $0.3 \leq x \leq 0.7$, results are reported elsewhere (Cheng, 2018). The XRD patterns of the solids with $x > 0$ show a shift of Bragg diffraction peaks indicating an increase of distances between the crystalline planes. The XRD patterns of Figure 2. show the anatase crystalline phases for both types of nanoparticles.

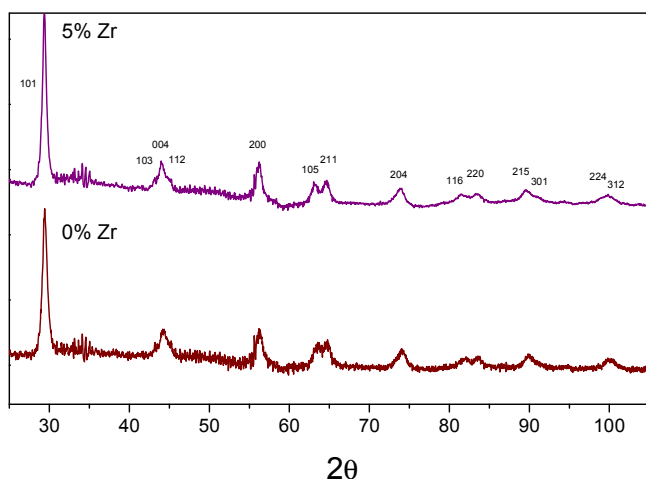


Figure 2: XRD patterns of nanoparticulate $Zr_xTi_{(1-x)}O_2$ solids with Zr content $x = 0$ and $x = 5\%$ heat treated during 4 hours at $410\text{ }^\circ\text{C}$.

The thickness of the coatings was measured by ICP technique consisting of measuring the mass of TiO_2 , covering the surface of a known quantity of glass beads, dissolved in an acid solution. The total mass of the deposited TiO_2 measured by ICP technique permitted to estimate the thickness of deposited TiO_2 layer to $\delta=8$ nm.

The BET measurements indicated a significant increase of the specific surface area from 25 m^2 when $x = 0$ to reach 70 m^2 as a maximum at $x = 0.05$. The high specific surface area could be explained by the material porosity. A TEM image of $Zr_{0.05}Ti_{0.95}O_2$ particles in Figure 3. evidences nanoporous morphology of the prepared solids.

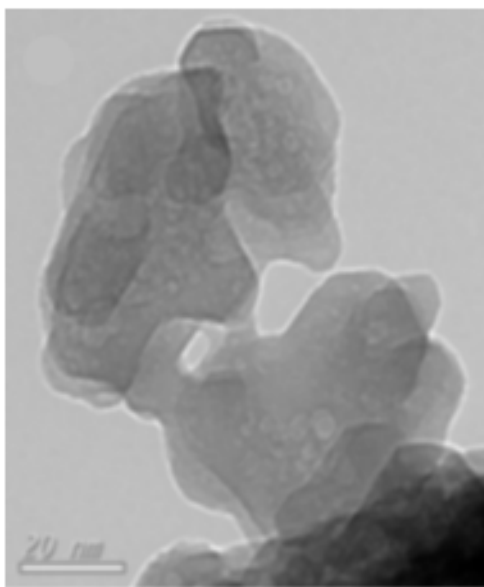


Figure 3: TEM image of nanoparticulate $Zr_{0.05}Ti_{0.95}O_2$ solids.

3.2 Photocatalytic activity on AMX abatement under solar irradiation

The solar irradiation power was measured for each experience. A typical UV solar irradiation pattern is presented on Figure 4. These measurements were used in order to calculate, by using equation (2) the solar

energy deposited per litre of treated solution. During our experiments the UV irradiation increased from 100 $\mu\text{W}/\text{cm}^2$ at 9,00 AM to 530 $\mu\text{W}/\text{cm}^2$ at noon then decreased to 99 $\mu\text{W}/\text{cm}^2$ at 5,00 PM.

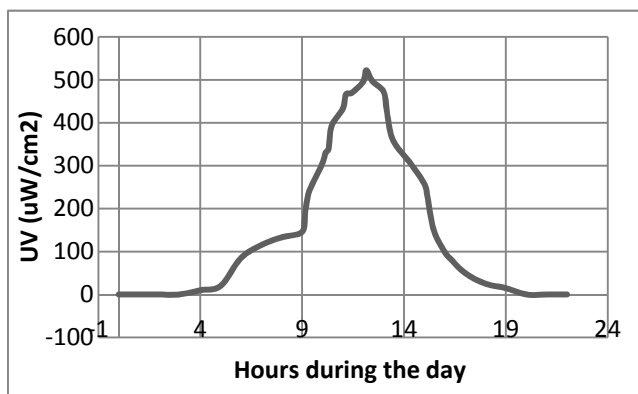


Figure 4: A typical UV solar irradiation pattern measured during the experimental days on the solar plant of University of Isfahan.

Solutions of 10 mg AMX dissolved in 10 L distilled water were submitted to solar irradiation. The pH was adjusted at 7.5 and H_2O_2 (100 mg/L) was added to the solutions. Results depicted in Figure 5. show the degradation of AMX increases in all cases by exposing the solution to solar irradiation. The photolysis alone is responsible for 22% degradation of AMX when the irradiation energy reaches 40 kJ/L. The degradation of AMX reached 39% by using glass beads coated with $\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_2$ particles. In contrast glass beads coated with TiO_2 show higher AMX degradation that reached 54% with an input energy of about 40 kJ/L. Comparative experiments with commercial TiO_2 powder were carried out at the same conditions as those of the coated TiO_2 . In each experience one gram of TiO_2 was added to 10 L of AMX solution. AMX degradation reached 65% at about 40 kJ/L. However the quantity of commercial TiO_2 used to obtain this higher AMX degradation is much higher than the quantity of TiO_2 coated on glass beads which has the advantage to be reused in next experiences.

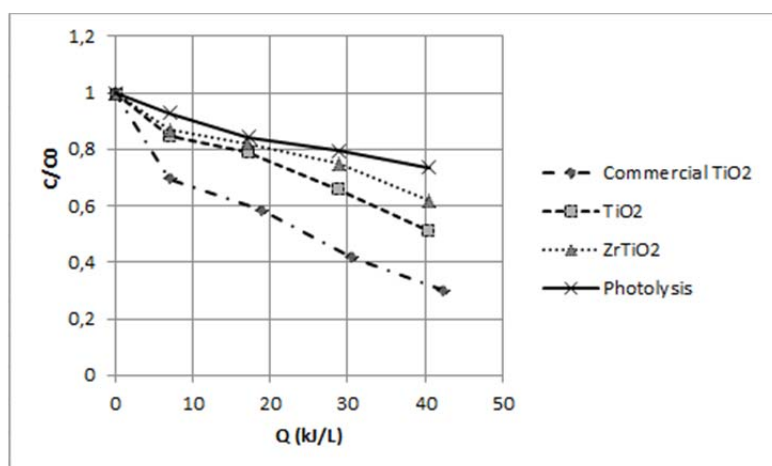


Figure 5: AMX abatement in 10L batch as a function of exposure to solar energy by using $\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_2$ and TiO_2 coated on glass beads compared with commercial TiO_2 and photolysis

4. Conclusions

TiO_2 photocatalysis is a promising technology due to its capability of using natural solar UV energy which can reduce the cost of associated with UV radiation production. The reactor used in this study has a compound parabolic collector that shows the best performance. In order to access the influence of solar irradiance, photocatalytic experiments were carried out for three types of catalyst. The $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$ photocatalysts ($X = 0$, $X = 0.05$) were prepared and the photocatalytic performance was studied on Amoxicillin elimination in a solar

photoreactor. Degradation percentage, after 240 min at the solar plant for commercial TiO_2 , TiO_2 and $\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_2$, were achieved 69, 48, 38, respectively in $\text{pH} = 7.5$. Results showed that only nearly 40 kJ/L of accumulated UV energy was necessary for these efficiencies. The Zr doping of TiO_2 shows lowering of the photocatalytic activity in our experimental conditions.

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