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STUDIES REGARDING PHOTOCATALYTIC DEGRADATION OF TWO DIFFERENT ORGANIC COMPOUNDS

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Abstract

Water has the most importance to human life, but the quality is very important. Due to rapid development of industrial activities, it has been contaminated with many organic compounds, which is a great concern for environmental quality and human health. Nowadays, the reduction of pollutants in water has attracted a great interest leading to development of Advanced Oxidation Processes (AOPs), among which TiO_2 heterogeneous photocatalysis, as a green and sustainable technology, is one of the most emerging and promising method. TiO_2 photocatalyst is known for its excellent ability of degradation and mineralization of organic pollutants.
In this work, it was studied the degradation process of Levetiracetam and 2,4,6, trichlorophenol in aqueous solution, by heterogeneous photocatalysis, in the presence of TiO_2 Aeroxide® P25, confirming its effectiveness. For Levetiracetam at 150 min degradation was about 80%, while 2,4,6, trichlorophenol was total mineralization.

Key words: *2,4,6 trichlorphenol degradation, Levetiracetam degradation, photocatalysis, titanium dioxide.*

INTRODUCTION

Over the last decades, water contamination with organic compounds has become an emerging environmental problem due to their continuous persistence in aquatic ecosystem (Ciobanu et al., 2013; 2014; Kadmi et al., 2015; Klavarioti et al., 2009; Rusu et al., 2014). Organic compounds discharged in the environment may impose toxicity on every rank of biological hierarchy. Apart from toxic effects, some of them may cause irreversible changes to the micro-organisms genome, making them resistant in their presence, even at low concentrations (Harja et al., 2011; Klavarioti et al., 2009). Some pollutants cannot be susceptible to biological treatments used in the wastewater treatment process because of their high chemical stability and low biodegradability.
Levetiracetam (LEV) is a tetrahydropyrrole with anticonvulsant activity and it shows good bioavailability (Schachter, 2000), linear pharmacokinetics, irrelevant protein binding, rapid achievement of steady-state concentrations (Patsalos, 2000; Perucca and Bialer, 1996), but the most important advantage of LEV is that presents no interaction with other antiepileptic drugs even at high dosage (Klitgaard et al., 1998).
2,4,6 trichlorophenol (2,4,6-TCP) is a chlorinated phenol, widely used in production of paper, pesticides, herbicide and wood preservatives (Noestheden et al., 2012). Their applications and releasing in water affects environmental quality and represent a great concern for human health.
One of the most efficient technologies in treatment of aqueous solutions for organic pollutants degradation is advanced oxidation processes (AOPs). In the last decades they have been applied for many organic compounds. AOPs such as ozonation, Fenton, photo-Fenton, ultrasound waves, sonochemical, photo-sonochemical processes, ultraviolet irradiation and sulfate radical-based oxidation (Krishnan et al., 2017; Safari et al., 2015). They are based on highly reactive transitory species such as H_2O_2, $OH\cdot$, O_2^-, O_3 for the complete mineralization of organic pollutants, pathogens and disinfection by-products. Among semiconductor catalysts TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS have the large efficiency in degrading (Chong et al., 2010).

Compared to conventional technologies, titanium dioxide (TiO_2) photocatalytic process the most emerging and promising (Dorian et al., 2011; Gómez de Castro et al., 2017). The advantages are ambient operating conditions, lack of mass transfer limitations, low operating costs and complete mineralization (Safari et al., 2015). TiO_2 photocatalyst is used in a large range of ambiguous refractory organic pollutants (Liu and Bi, 2017; Madjene et al., 2013). The organic substances are reduced to CO_2, H_2O and inorganic ions, all of them harmless for the ecosystem (Pourmoslemi et al., 2016). On the surface of TiO_2 photocatalyst are induced reductive and oxidative reactions (Atitar et al., 2015; Nutescu Duduman et al., 2018).

The objective of this work was to investigate the potential of TiO_2 heterogeneous photocatalysis for the removal of two different category of refractory pollutant: LEV and 2,4,6 – TCP.

MATERIALS AND METHODS

Chemicals

2,4,6-trichlorophenol (99%) and levetiracetam (≥98%) were purchased from Sigma-Aldrich Co and used without further purification.

Titanium dioxide, Degussa P25 (80% anatase, 20% rutile; Sigma Aldrich, France) was used as photocatalyst for this study.

Solutions were prepared using ultra-pure water.

Table 1. Pollutant characterization

Pollutant	Molecular formula	Molecular weight (g/mol)	Log $K_{o/w}$	pKa
2,4,6 Trichloro-phenol	$C_6H_2Cl_3OH$/ $C_6H_3Cl_3O$	197.45	3.69	6.19
Levetiracetam	$C_8H_{14}N_2O_2$	170.21	-0.49 (est)	16.09

Methods

Experiments for the degradation of LEV were conducted in a batch reactor (a glass beaker), mechanistically stirred by using a mechanic stirrer with four blades and adjustable speed, with external irradiation by two outer low-pressure fluorescent lamps (Philips PL-S 9W/10/2P lamps) whose main emission peak was the UV region (λ=365 nm). The radiation intensity was measured by a radiometer Delta Ohm DO9721 with an UVA probe.

The system employed in this work for studying the degradation of LEV consist of a rectangular enclosure, with a length of 100.2 cm and a width of 40.2 cm (Favier et al., 2015).

The tests were carried out at room temperature and at solution natural pH.

The experiments for the photodegradation of 2,4,6-TCP were conducted in a cylindrical borosilicate glass reactor. A mercury vapour lamp, which maximal emission was at 365 nm (Philips PL-S 9W/10/4P) was used as UV light source, placed in a Pyrex tube and disposed axially inside the reactor. Experiments were conducted at room temperature (20 ± 2°C) and at natural pH. The aqueous solution was magnetically stirred before and during irradiation for the catalyst suspension. The incident light intensity for the photodegradation assays was measured by VLX-3W radiometer (Vilber Lourmat, France).

The aqueous solutions were prepared by dissolving a well-known amount of compound in ultrapure water, without adjusting the pH before and during the degradation process. Subsequently, a specific amount of TiO_2 was dispersed in the solution. Before the irradiation, the suspension was stirred in the dark for 30 min to achieve the adsorption-desorption equilibrium. For the photocatalytic experiments, was considered an irradiation time of 140 and 160 minutes for the degradation of LEV and 2,4,6-TCP, respectively. Samples were taken at regular time intervals and filtered through a polymer syringe filter (Minisart/Sartorius) of 0.45 μm of porosity to separate the photocatalyst (Favier et al., 2016).

Pollutant concentration was measured by high performance liquid chromatography (HPLC), using a WATERS ACQUITY UPLC® system equipped with a diode array detector. A Waters Symmetry® C18 Column (250 x 4.6 mm, 5 μm) was used for analyte separation. The mobile phase was a mixture of acetonitrile/water/formic acid (60/40/0.1 for 2,4,6-TCP and 10/90/0.1 for LEV, respectively). Analysis was carried out under isocratic mode with a flow rate of 1 ml/min and a injected volume of 50 μL. 2,4,6-TCP was detected at 285.8 nm; its retention time was of 9.5 minutes. LEV was detected at 210.2 nm and the retention time was 8.3 minutes.

RESULTS AND DISCUSSIONS

The initial pollutant concentration (C_0) has a major influence in the photocatalytic degradation. The effect of initial LEV concentration was studied by varying the initial LEV concentration in the range 4.5 - 18 mg/L at 1 g/L TiO_2 loading, at ambient temperature, maximal irradiation flux and a stirring rate of 555 rpm, with an irradiation time of 150 min. The results showed that with increasing the pollutant concentration, degradation rate decreases. Degradation profile indicates that the optimal removal of LEV it's at 4.5 mg/L. The degradation efficiency at 150 min decreased from 99% to 76% with increasing LEV concentration from 4.5 to 18 mg/L.

A possible explanation for this behavior can be that the path length of photons entering the solution decreases with increasing the initial concentration of pollutant. The reverse effect is observed in low concentration, thus increasing the number of photon absorption by the TiO_2 in lower concentration, in accord with literature (Lutic et al., 2017; Tayade, 2009).

The effect of initial 2,4,6-TCP concentration on the degradation reaction was tested in same conditions with LEV. All experiments were realized without pH regulation and an irradiance of 59.6 W/m^2.

The catalyst efficiency is strongly affected by 2,4,6-TCP initial concentration. Thoroughly, a degradation yield of 81.5% was obtained for an initial pollutant concentration of 2 mg/L after 15 minutes of UV irradiation, compared to only 33.4 % for a concentration of 18 mg/L (Figure 1). Similar results were reported by Dionysiou et al. (2000) for the photodegradation of 2,4,6-TCP using a bench-scale TiO_2 rotating disk reactor.

A explanation for this comportment can be that when pollutant concentration increases, the vacant sites on TiO_2 surface is reduced by the organic surface adsorption on the catalyst surface, leading to an obstruction of the light penetration having an arousing effect on hydroxyl radicals generation and target pollutant oxidation. Therefore, this persuade to a decrease in pollutant degradation (Renata et al., 2005).

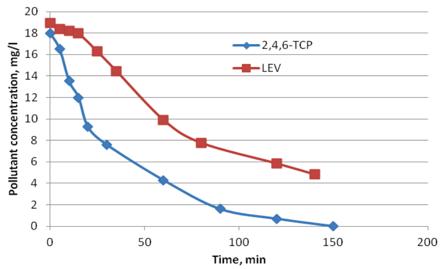

Figure 1. Degradation efficiency of 2,4,6-TCP and LEV in aqueous solution with TiO_2 P25 (1 g/L), natural pH and UV irradiance

CONCLUSIONS

In this paper was investigated the efficiency of TiO_2 photocatalyst on degradation of organic compound 2,4,6-TCP and LEV. The experiments were conducted at laboratory scale, in batch reactors using TiO_2 Aeroxide P25 as photocatalyst. The results shown that titanium dioxide photocatalytic process is a very promising method for the removal of refractory organic pollutants (giving their high chemical stability) and confirms the applicability of heterogeneous photocatalysis on environmental pollution issues.

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