

# Electron acceptors effect on photocatalytic degradation of metformin under sunlight irradiation

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## ABSTRACT

The water purification is a serious issue especially with the unprecedented growth of pollutants from pharmaceutical industries. The metformin, an antidiabetic drug, is one of pharmaceutical pollutants that can be found in domestic and hospital wastewater which are suspected to affect the balance of ecosystems and the human health even at low concentrations. In this paper, we study the metformin elimination from wastewater using heterogeneous photocatalysis. We investigate the metformin degradation in aqueous medium under sunlight irradiation in the presence of titanium dioxide (TiO<sub>2</sub>) Degussa P25 (80% anatase, 20% rutile) as catalyst and in a semi-pilot solar reactor. Contrary to existing works, we use electron acceptors such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), potassium persulphate K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and sodium persulphate Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to improve the TiO<sub>2</sub> photocatalytic activity. Different TiO<sub>2</sub> photocatalysts were used (P25, EL10, DT51, PC105, PC500 and T42) for preliminary study before selecting P25. The solar reactor was (i) set facing south and (ii) a peristaltic pump is used to re-circulate the treated mixture between the reactor and the reservoir in a closed circuit. During sunlight irradiation, the solution of metformin was homogenized by magnetic stirrer. The degradation was monitored by measuring the metformin concentration using a UV-visible spectrophotometer at wavelength of 236 nm. The used photocatalysts were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The average crystallite size was estimated using X-ray diffraction. The experimental results showed that metformin degradation rate in presence of electron acceptors was increased significantly during photocatalysis compared to photolysis and adsorption. The apparent rate constant of every reaction involved was evaluated and the kinetics of degradation was described by the Langmuir-Hinshelwood (L-H) model.

## 1. Introduction

Access to clean water and sanitation is one of the most important problems affecting people over the world. Recently, many researchers have been interested in water purification in order to reduce the purification cost and the use of chemical compounds (Borges et al., 2016; Blanco et al., 2015; Gomez et al., 2013; Fuchs et al., 2009; Yamaguchi et al., 2010). The first detection of drugs in surface waters was in 1976, when a concentration of 1 µg/L of clofibric acid, a drug used against cholesterol, and another of 2 µg/L of salicylic acid were detected in the Nevada Lake, US. However, it did not receive much attention until 1992, where German researchers detected clofibric acid in the drinking water in Berlin. Since then, different categories of pharmaceuticals have been found in surface waters (Halling-Sorensen et al., 1998; Kümmeler, 2003). Metformin is an antidiabetic drug with one of the highest consumption rates of pharmaceuticals worldwide. Metformin is part of the essential drugs list of the World Health Organization (updated list in

April 2013) (WHO). It is released in considerable amounts of up to several tens of µg/L into recipient rivers, due to its high influent concentrations of up to 100 µg/L and its high, but incomplete, degradation (Scheurer et al., 2012). In this paper, we focus on the degradation of metformin using heterogeneous photocatalysis.

Heterogeneous photocatalysis is a phenomenon in which the catalyst initiates a chemical reaction by the action of solar energy, in the presence of a photocatalyst, light and water. This process is based on the generation of hydroxyl radical HO<sup>•</sup>. This species is a strong oxidant which is capable of converting organic substances to harmless compounds (carbon dioxide and water) (Chen and Cao, 2005; Vaiano et al., 2015). Early works on water purification using heterogeneous photocatalysis have, mainly, focused on the photo-mineralization of organics dissolved in aqueous solution employing the semiconductor in the form of a powder suspension. The photocatalytic treatment has been proven to be an effective method of water decontamination (Chen and Cao, 2005; PARSONS, 2004). The use of solar energy to degrade pollutants

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Nomenclature		t	time (min)
$\lambda$	wavelength (nm)	k	reaction rate constant ( $\text{min}^{-1}$ )
$\nu$	frequency ( $\text{s}^{-1}$ )	Acronyms	
$h$	plank's constant (eV-s)		
$e^-$	electron (dimensionless)	SEM	scanning electron microscopy
$h^+$	hole (dimensionless)	XRD	X-ray diffraction
$C_0$	initial metformin concentration (mg/L)	Met	metformin
$C$	concentration of metformin at any time (mg/L)		

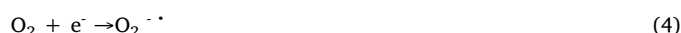
by photocatalysis represents an economic and sustainable alternative to degrade pollutants (Borges et al., 2016; Blanco et al., 2015).

Since Fujishima and Honda (Fujishima et al., 1969) reported the photocatalytic hydrolysis of water under the UV light radiated titanium dioxide ( $\text{TiO}_2$ ), the photocatalytic property of this material has received a special focus (Fujishima et al., 1999). Titanium dioxide ( $\text{TiO}_2$ ) is one of the most used semiconductor materials that has been employed as a photocatalyst for water purification in recent years (Vaiano et al., 2015; Naldoni et al., 2012; Du et al., 2013; Yang et al., 2009; Vaiano et al., 2014; Belver et al., 2009), due to its high activity in the photo-degradation of organic compounds related to the strong oxidation potential of the holes excited by the UV light in the valence band (Leinsebliger et al., 1995), low cost, low toxicity, and chemical stability (Gomez et al., 2013; Fuchs et al., 2009; Yamaguchi et al., 2010; Saquib et al., 2008; Duxbury, 1993; Hoffman et al., 1995). It has been reported that the use of  $\text{TiO}_2$  in suspension is efficient and is mainly related to the large nanoparticles surface area and the proximity between nanoparticles surface and pollutant species (Martins et al., 2016). The titanium dioxide is found in three different crystal structures: anatase, brookite and rutile (Blanco et al., 2015; Gopal et al., 1997).

The  $\text{TiO}_2$  acts as an initiator for light induced redox reactions because of its electronic structure characterized by an electron filled valence band and empty conduction band (Leinsebliger et al., 1995). The initial step in  $\text{TiO}_2$ , mediated photocatalysis under irradiation of light with wavelength lower than  $\lambda \leq 400 \text{ nm}$ , involves the generation of electron/hole pairs ( $e^-/h^+$ ), which results from the passage of an  $e^-$  from the valence band to the conduction band (Hoffman et al., 1995; Herrmann, 2005) as shown in Fig. 1.

The formed hole in the valence band and the excited electron in the conduction band are capable of undergoing redox reactions with adsorbed reactants (Leinsebliger et al., 1995). The electron reacts with

oxygen provided from the air and adsorbed on the surface of  $\text{TiO}_2$ . Hydroxyl radicals ( $\text{HO}^\cdot$ ) which are highly oxidizing and responsible for pollutants degradation are generated by the hole. Resulting in the formation of hydroxyl radicals ( $\text{HO}^\cdot$ ), superoxide radical anions ( $\text{O}_2^{\cdot-}$ ), and hydroperoxyl radicals ( $\text{OOH}^\cdot$ ) as shown below (Daneshvar et al., 2003; Dionysiou et al., 2000; Da Silva and Faria, 2003):



Organic pollutants are attacked and oxidized by the hydroxyl radicals formed through the above mechanisms. In addition, superoxide radical anions, and in some cases positive holes, can be used as possible oxidizing species that can attack organic contaminants present at, or near, the surface of  $\text{TiO}_2$  (Zang and Farnood, 2005). These radicals react on organic pollutants leading to their oxidation until total mineralization.

In this present paper, we focus on the degradation of metformin by using a suspension of titanium dioxide under sunlight irradiation in a semi-pilot solar reactor. We use various electron acceptors to improve the photocatalytic activity of  $\text{TiO}_2$  because of their higher oxidation potential than oxygen and an interesting property of generating reactive species such as  $\text{HO}^\cdot$ ,  $\text{O}_2^{\cdot-}$  and  $\text{SO}_4^{\cdot-}$ . In addition, electron acceptors are more effective thermodynamically than oxygen. From the literature, it has been reported that the oxidation potential of different electron acceptors used in this work, were:  $E(\text{H}_2\text{O}_2/\text{HO}) = -827 \text{ mV}$ ,  $(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{\cdot-}) = 2 \text{ V}$  and  $E(\text{O}_2/\text{O}_2^{\cdot-}) = -155 \text{ mV}$  for oxygen (Faisal et al., 2007; Vanýsek, 2007).

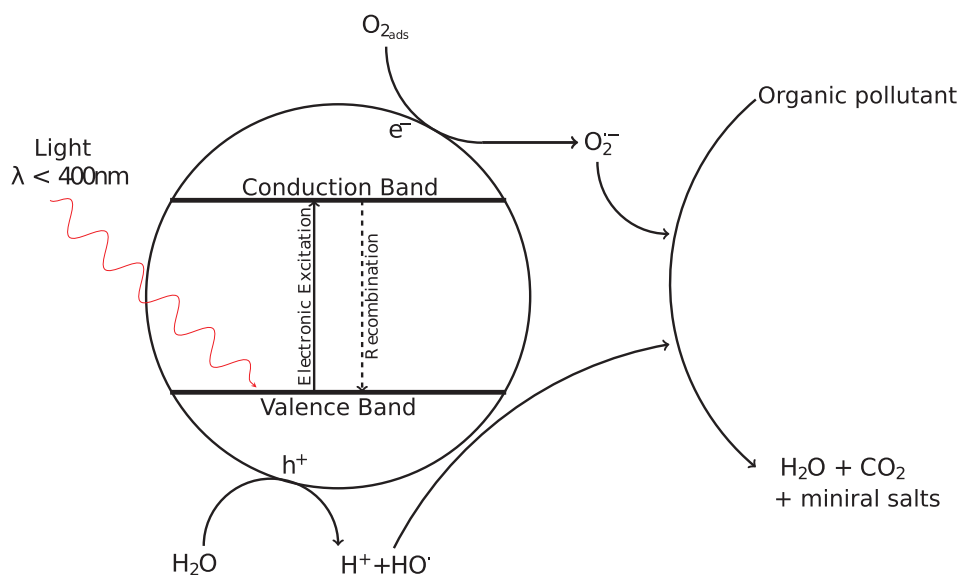


Fig. 1. Principle of heterogeneous photocatalysis of a spherical titania particle (semiconductor  $\text{TiO}_2$ ).

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