

## Comparison of TiO<sub>2</sub> and ZnO catalysts for heterogenous photocatalytic removal of vancomycin B

Giusy Lofrano<sup>1</sup>, Can Burak Özkal<sup>2</sup>, Maurizio Carotenuto<sup>1</sup> and Süreyya Meriç<sup>\*2</sup>

<sup>1</sup>Department of Chemistry and Biology- University of Salerno- via Giovanni Paolo II,  
132- 8484 Fisciano (SA), Italy

<sup>2</sup>Tekirdağ Namik Kemal University Environmental Engineering Department Çorlu, Tekirdağ, Turkey

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**Abstract.** Continuous input into the aquatic ecosystem and persistent structures have created concern of antibiotics, primarily due to the potential for the development of antimicrobial resistance. Degradation kinetics and mineralization of vancomycin B (VAN-B) by photocatalysis using TiO<sub>2</sub> and ZnO nanoparticles was monitored at natural pH conditions. Photocatalysis (PC) efficiency was followed by means of UV absorbance, total organic carbon (TOC), and HPLC results to better monitor degradation of VAN-B itself. Experiments were run for two initial VAN-B concentrations (20-50 mgL<sup>-1</sup>) and using two catalysts TiO<sub>2</sub> and ZnO at different concentrations (0.1 and 0.5 gL<sup>-1</sup>) in a multi-lamp batch reactor system (200 mL water volume). Furthermore, a set of toxicity tests with *Daphnia magna* was performed to evaluate the potential toxicity of oxidation by-products of VAN-B. Formation of intermediates such as chlorides and nitrates were monitored. A rapid VAN-B degradation was observed in ZnO-PC system (85% to 70% at 10 min), while total mineralization was observed to be relatively slower than TiO<sub>2</sub>-PC system (59% to 73% at 90 min). Treatment efficiency and mechanism of degradation directly affected the rate of transformation and by-products formation that gave rise to toxicity in the treated samples.

**Keywords:** photocatalysis; vancomycin B; degradation; mineralization; ecotoxicity; transformation by-products; TiO<sub>2</sub>; ZnO

### 1. Introduction

Antibiotics are released into aquatic environment by different pathways since they are among the most frequently prescribed pharmaceuticals in human and veterinary treatment of bacterial infections. Due to their continuous input into the aquatic ecosystem at lower inhibitory concentrations of antibiotics gives a rise to growing potential for the development of antimicrobial resistance (Varela *et al.* 2013, Sharma *et al.* 2016, Lofrano *et al.* 2017, Inyinbor *et al.* 2018).

Several treatment alternatives have been attempted to remove antibiotics. Literature studies showed that photocatalysis process using TiO<sub>2</sub> or ZnO nanoparticles enables to degrade effectively antibiotics in suspended (Chatzitakis *et al.* 2008, Elmolla and Chaudhuri 2010, Dimitrakopoulou *et al.* 2012, Lofrano *et al.* 2014, 2016, Ozkal *et al.* 2016, Vaiano *et al.* 2015, Van Doorslaer *et al.*

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\*Corresponding author, Professor, E-mail: smeric@nku.edu.tr

2015). The recent study by Lofrano *et al.* (2014) has been a specific one handled photocatalytic treatment of Vancomycin B (VAN-B) using TiO<sub>2</sub> catalyst under 50 mgL<sup>-1</sup> VAN-B initial concentration and at a light intensity of  $4.5 \times 10^{-7}$  Einstein s<sup>-1</sup> using 0.1 and 0.2 gL<sup>-1</sup> TiO<sub>2</sub> doses. The authors assessed by-products formation and a multi battery toxicity to *Daphnia magna*, *Pseudokirchneriella subcapitata* and *Ceriodaphnia dubia* specie. However there is still a need to study various process conditions to remove VAN-B by photocatalysis since it was associated with antibiotic resistance as well (Wilson *et al.* 2002, Varela *et al.* 2013). Furthermore, comparative photocatalytic removal of antibiotics are still limited using TiO<sub>2</sub> and ZnO (Palominos *et al.* 2009).

The present study was designed to determine comparative photocatalytic degradation kinetics and mineralization of VAN-B at two initial doses and two catalysts doses and types (TiO<sub>2</sub> and ZnO) and at natural pH of solution. Furthermore, a set of toxicity tests with *Daphnia magna* was performed to evaluate the detoxification potential of VAN-B and toxicity of oxidation by-products formed during photocatalysis experiments. Additionally, the TiO<sub>2</sub> in treated solutions was removed in order to avoid any possible interference with the analytical measurements.

## 2. Materials and methods

### 2.1 Chemicals and reagents

TiO<sub>2</sub> (CAS #13463-67-7, zero charge point of 6.8 and specific surface areas of 35-65 m<sup>2</sup>/g (BET) (Sigma Aldrich, 21 nm, CAS: 13463-67-7) was purchased from Sigma- Aldrich while Zinc oxide (ZnO) was provided from Merck (CAS Number 1314-13-2; Catalog No: 8849) with a specific surface area of 47 m<sup>2</sup>/g (BET) and mean particle size of 230 nm. HPLC grade water and methanol were supplied from Sigma Aldrich and used as received. VAN-B was supplied from a pharmaceutical producer industry as analytical grade. VAN-B is a glycopeptide antibiotic, comprises of three ionizable phenol groups (pKa=7.2, 8.6 and 9.6), one carboxylic acid group (pKa=2.9) and two aminogroups (pKa 10.4 and 12.7), and six secondary alcohol groups (Harris *et al.* 1983, Lofrano *et al.* 2014).

### 2.2 Experimental set-up

The experiments were performed in a batch reactor system (200 mL water volume) using a photo reactor equipped with a multi lamp system (14 lamps, Philips-8W) in 350 nm wavelength. The details of photo reactor are described elsewhere (Özkal *et al.* 2016). The incident of photo flux, measured by Universal Photometer (MRC Model YK-37UVSD) as 49.4 Wm<sup>-2</sup>. The temperature of reaction solutions was maintained at  $25 \pm 0.5$  °C by with an integrated ventilation system.

Freshly prepared VAN-B solutions (20 mgL<sup>-1</sup> and 50 mgL<sup>-1</sup>) were transferred into a glassware with 200 mL effective volume (<5 cm water depth) and put in the photo-reactor. Before starting the photocatalysis process, the suspensions consisting of antibiotics solution with defined catalyst dose, were sonicated for 10 min by using a MRC Ultrasonic bath. After that dark (adsorption) experiments were carried out in the photocatalytic reactor and at the same conditions of photocatalysis but the lamps were switched off. Additionally, effect of photolysis and hydrolysis followed by photolysis process on VAN-B removal were also studied.

Photocatalytic experiments were run *versus* time (from 5 to 120 min) using TiO<sub>2</sub> and ZnO at two loading ratios (0.1 and 0.5 gL<sup>-1</sup>). All photocatalytic experiments were carried out at natural pH

of the VAN-B solutions (pH=5.5). Finally, effluent was droplet filtered using Millex HA MF Milipore mixed cellulose (REF: SLHA033SS/ LOT: R2KA49112) cut off filter (0.45 µm) to separate catalysts in the treated samples.

### 2.3 Analytical procedures

The concentration of VAN-B was monitored by HPLC-UV (Finnigan Surveyer) equipped with a reversed phase C18 analytical column (Vydac, 5 µm, 150 mm ×3.0 mm). The compounds were separated using as mobile phase a mixture of methanol/ultrapure water (35%/65%) at flow rate of 1 mL min<sup>-1</sup>. The injection volume was 10 µL and the wavelength set for the quantification was 281 nm according to the maximum light absorption of the VAN-B (Berthod *et al.* 1996, Lofrano *et al.* 2014). The limit of quantification (LOQ) of this method was 0.5 µg L<sup>-1</sup>. The UV-vis absorbances were recorded using a spectrophotometer (Schimadzu 1800 Lamda). The wavelengths at 281 nm (UV<sub>281</sub>) and at 254 nm (UV<sub>254</sub>) were recorded in accordance with Lofrano *et al.* (2014), as indicators of aromaticity and C=C double bond, respectively. Chlorides and nitrates were determined by Ion Chromatogram (Dionex 2000). TOC was measured using a Shimadzu TOC-L CPN analyzer. The limit of determination (LOD) and quantification (LOQ) of this method was between 0.01-0.05 ppb.

### 2.4. Acute toxicity

Acute toxicity of raw and photocatalytic treated samples was assessed on freshwater crustaceans *Daphnia magna* according to ISO 6341 Method (2012). Toxicity tests were performed quadruplicate using five new born daphnids (<24 h) in each test beaker with 50 ml effective volume. A negative control test was performed in parallel to control the quality of test organisms (<5% of immobilization). Daphnids were grown in the laboratory at 16 h day light-8 h dark periods supplying a 3000 lux illumination at 20°C room temperature. Daphnids were fed with unicellular green algae (*Selenastrum capricornutum*, 300,000 cells.mL<sup>-1</sup>) and baker's yeast (*Schizosaccharomyces cerevisiae*, 200,000 cells.mL<sup>-1</sup>). Samples were diluted at 50% using standard solution and pH was set at 8. Results were expressed as a percentage of immobilised animals after 24 h. and 48 h exposure times according to Eq. (1).

$$\% \text{immobilization} = (\text{Number of immobilized organisms}) / \text{Total number of test organisms} \quad (1)$$

The significance of differences between average values of different experimental treatments and controls was assessed by the analysis of variance (ANOVA) considering a significance threshold level always set at 5%. When ANOVA revealed significant differences among treatments, post-hoc tests were carried out with Tukey's test. Statistical analyses were performed using Microsoft Excel2013/XLSTAT©-Pro (Version7.2, 2003, Addinsoft, Inc., Brooklyn, NY, USA).

## 3. Results and discussion

### 3.1 Dark adsorption

It was reported that dark adsorption did not affect the degradation of VAN-B at natural pH (5.5) after 120 min (Lofrano *et al.* 2014). The similar result was observed under the experimental

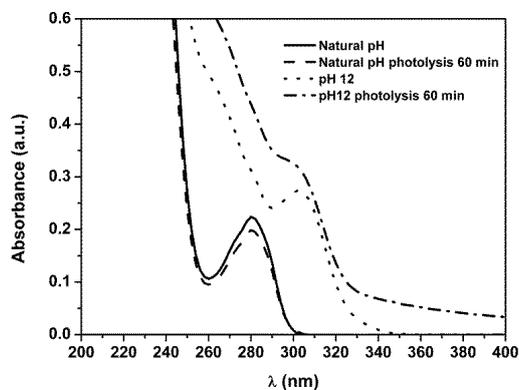


Fig. 1 Change of VAN-B structure for different pH values

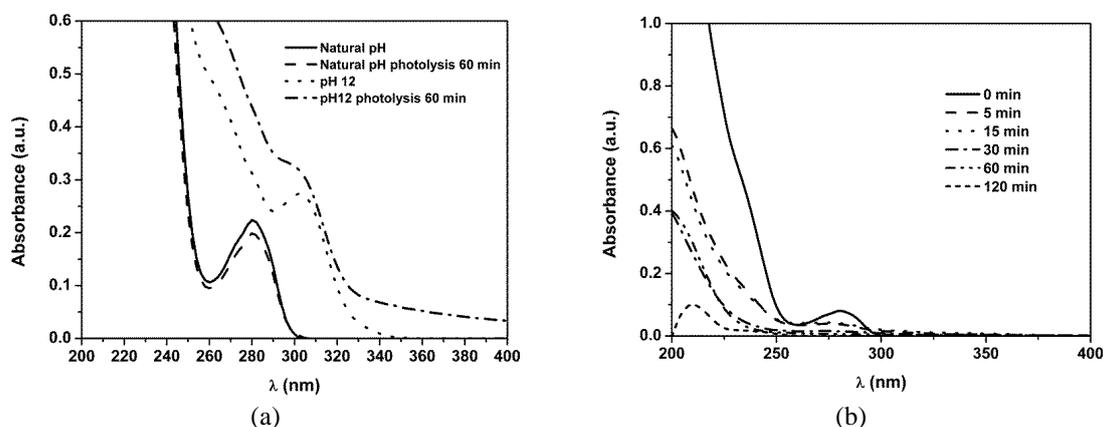


Fig. 2 UV absorbance removal of 20 mgL<sup>-1</sup> VAN-B by photocatalysis process as a function of irradiation time using 0.1 gL<sup>-1</sup> (a) and 0.5 gL<sup>-1</sup> (b) TiO<sub>2</sub> respectively

condition in this study (<5% removal) in accordance with the other studies run on different antibiotics (Giraldo *et al.* 2010, Nosrati *et al.* 2012, Ozkal *et al.* 2016). Thus, presonicated catalysts were directly contacted with VAN-B solutions during photocatalysis experiments.

### 3.2 Photolysis

As seen in Fig. 1 photolysis was not found effective to remove VAN-B (<5% of removal at 281 nm) in accordance with the previous findings on VAN-B (Lofrano *et al.* 2014) and other antibiotics (Elmolla and Chaudhuri 2010, Ozkal *et al.* 2016).

### 3.3 Hydrolysis/photolysis

As increasing pH to 12, it was possible to observe a sharp increase in the absorbance values of VAN-B (indicator bands of aromatic structure) that shifted peak absorbance from 287 to 315 nm wavelength. Furthermore, the absorbance increased after photolysis during 60 min (Fig. 1). Thus, sequential photocatalysis experiments were performed at natural pH value.

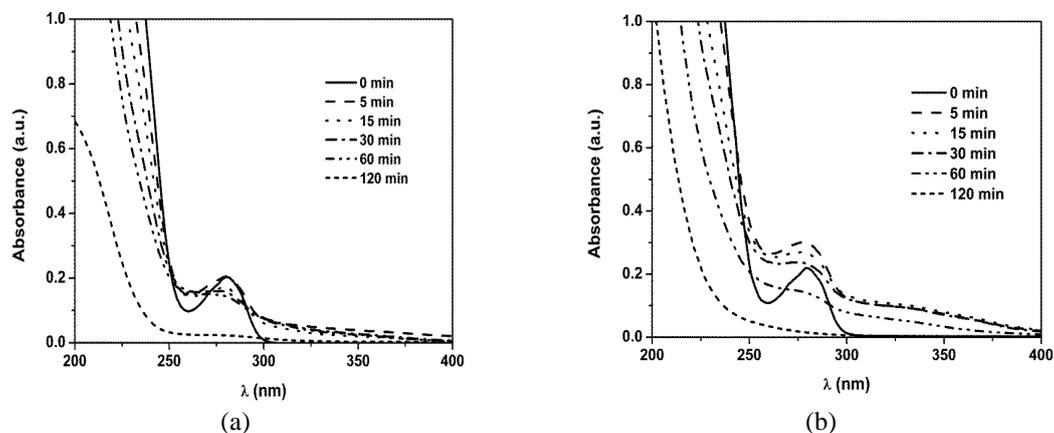


Fig. 3 Photocatalytic UV absorbance removal of 50 mgL<sup>-1</sup> VAN-B using (a) 0.5 gL<sup>-1</sup> TiO<sub>2</sub> and (b) 0.5 gL<sup>-1</sup> ZnO

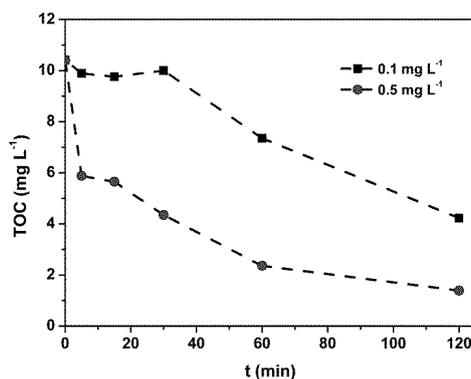


Fig. 4 Photocatalytic mineralization of 20 mgL<sup>-1</sup> VAN-B as a function of irradiation time using 0.1 gL<sup>-1</sup> and 0.5 gL<sup>-1</sup> TiO<sub>2</sub> respectively

### 3.4 Degradation of VAN-B by photocatalysis

As displayed in Fig. 2, the degradation by-products occurred. The value UV<sub>254</sub> increased when 0.1 gL<sup>-1</sup> TiO<sub>2</sub> concentration was used (Fig. 2(a)). As expected, increasing TiO<sub>2</sub> dose to 0.5 gL<sup>-1</sup> promoted the photocatalytic oxidation of 20 mgL<sup>-1</sup> VAN-B and any by product formation was not evidenced at UV<sub>254</sub> absorbance (Fig. 2(b)).

The formation of aromatic organic intermediates at wavelengths close to 280 nm affecting the corresponding value, was observed during photocatalytic treatment in our previous study (Lofrano *et al.* 2014). Although by-products formation was more evident in the UV profile of the ZnO system both TiO<sub>2</sub> and ZnO were found to be efficient catalysts to photo-oxidize 50 mgL<sup>-1</sup> VAN-B during 120 min irradiation as seen in continuous decreasing UV profile versus time shown in Fig. 3.

### 3.5 Mineralization of VAN B by photocatalysis and assessment of kinetics

Contrary to UV profiles evolved, a gradual decrease in TOC was observed although the

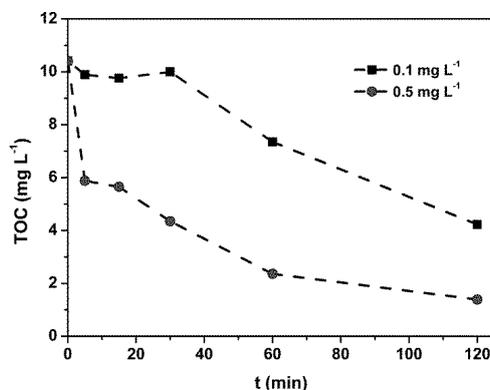


Fig. 5 Photocatalytic mineralization of 50 mgL<sup>-1</sup> VAN-B as a function of irradiation time using (a) 0.5 gL<sup>-1</sup> TiO<sub>2</sub> and (b) 0.5 gL<sup>-1</sup> ZnO respectively

mineralization was very slow due to longer stabilization time needed to degrade the by-products (Dimitrakopoulou *et al.* 2012). In the case of 20 mgL<sup>-1</sup> VAN-B initial concentration, a 60% and 87% of TOC removals were obtained using 0.1 gTiO<sub>2</sub>L<sup>-1</sup> and 0.5 gTiO<sub>2</sub>L<sup>-1</sup> concentrations respectively during 120 min of oxidation (Fig. 4).

When initial VAN-B concentration was increased to 50 mgL<sup>-1</sup>, ZnO achieved an 85% of VAN-B removal in the first 10 min. The photo-oxidation was faster than TiO<sub>2</sub> system that could perform only a 70% of VAN-B removal at the same time (Fig. 5). This result is in accordance with Chatzitakis *et al.* (2008) who reported that ZnO resulted in the best catalysts leading after 90 min of treatment to almost complete (90%) degradation of 50 mgL<sup>-1</sup>CAP among different catalysts used at 1 gL<sup>-1</sup> concentration. However, a lower mineralization was achieved using ZnO (59% removal) than TiO<sub>2</sub> conditions (73% TOC removal) that TiO<sub>2</sub> showed better activity for the photocatalytic degradation of a large number of organic compounds as reported elsewhere (Elmolla *et al.* 2010, Giraldo *et al.* 2010, Nosrati *et al.* 2012). It can be explained that while by-products formation during initial parent compound degradation higher ZnO surface area become occupied by increased load of degradation by-products thereby results with reduced efficiency of TOC removal (Palominos *et al.* 2009).

### 3.6 Degradation and mineralization kinetics

Because of by-products formation it was not possible to calculate the degradation kinetics on the basis of UV removal. The kinetics of photocatalytic mineralization is handled according to Langmuir-Hinselwood (L-H) model as described elsewhere (Lofrano *et al.* 2014). Since for dilute solutions the adsorption coefficient  $K$  is  $\ll 1$  just as the case pharmaceuticals that exist at very low concentrations in receiving water environment, the L-H equation simplifies to the following Eq. (1) as named pseudo-first-order kinetic equation

$$R = -\frac{dC}{dt} = kC \quad (2)$$

where  $R$  is the pseudo-first-order rate,  $C$  is the concentration of target organic compound,  $t$  is being the process time (min) and  $k$  is the reaction rate constant. The integration of Eq. (2) between initial time ( $t_0 = 0$  min) and “ $t$ ” results in the following Eq. (3)

Table 1 Photocatalytic degradation and mineralization rate kinetics of 20 mg L<sup>-1</sup> VAN-B at different conditions (pH: 5.5; irradiance: 49.4 Wm<sup>-2</sup>)

Kinetics coefficients	0.1 g L <sup>-1</sup> TiO <sub>2</sub>	0.1 g L <sup>-1</sup> TiO <sub>2</sub>	0.5 g L <sup>-1</sup> TiO <sub>2</sub>	0.5 g L <sup>-1</sup> TiO <sub>2</sub>
	$k_{\text{VAN-B}}$	$k_{120 \text{ TOC}}$	$k_{\text{VAN-B}}^{*1}$	$k_{120 \text{ TOC}}$
$k$ (min <sup>-1</sup> )	0.098	0.0073	0.152	0.0149
$R^2$	0.983	0.980	0.805	0.910
$t_{1/2}$ (min)	7.06	94.9	9.01	46.51
50 mg L <sup>-1</sup> VAN-B				
Kinetics coefficients	0.5 g L <sup>-1</sup> TiO <sub>2</sub>	0.5 g L <sup>-1</sup> TiO <sub>2</sub>	0.5 g L <sup>-1</sup> ZnO	0.5 g L <sup>-1</sup> ZnO
	$k_{\text{VAN-B}}^{*2}$	$k_{120 \text{ TOC}}$	$k_{\text{VAN-B}}^{*2}$	$k_{120 \text{ TOC}}$
$k$ (min <sup>-1</sup> )	0.052	0.0095	0.066	0.0069
$R^2$	0.96	0.89	0.92	0.918
$t_{1/2}$ (min)	13.25	72.96	10.50	100.45

\*1: Representing 0-30 min of process duration

\*2: Representing 0-60 min of process duration

$$-\ln \left( \frac{C}{C_0} \right) = kt \quad (3)$$

where  $C_0$  is UV<sub>254</sub> or UV<sub>281</sub> at initial time (untreated VAN-B solution) and  $k$  is the kinetic constant (L min<sup>-1</sup>). A plot of Eq. (3) gives a straight line with a slope of  $k$ . The half-life of a first-order reaction is independent of the starting concentration and is given by

$$t_{1/2} = \ln 2 / k \quad (4)$$

In accordance with the literature the experimental data obtained in this study well fitted pseudo first order kinetics (Lofrano *et al.* 2014, Vaiano *et al.* 2015). Accordingly, Table 1 shows  $k$  and  $t_{1/2}$  calculation results with correspondent regression ( $R^2$ ) values for all investigated catalyst loadings. Obviously, the  $k$  value increased when TiO<sub>2</sub> concentration increased. Regarding the variation in  $t_{1/2}$ , it can be demonstrated that VAN-B was rapidly degraded to intermediates while mineralization took much longer time, indicating that intermediates formed needed long time to be completely oxidized (Lofrano *et al.* 2014, 2016, Sapiano *et al.* 2015).

If two catalysts are compared for 50 mgL<sup>-1</sup> VAN-B removal it is seen that ZnO favoured to oxidize VAN-B better than TiO<sub>2</sub> with a higher  $k_{\text{VAN-B}}$  value and shorter  $t_{1/2}$  time. However, it is worth noting that the intermediates formed were not removed as much as effectively by ZnO system although it has a larger surface area to lead a higher adsorption capacity (Elmolla and Chaudhuri 2010).

### 3.7 Formation of by-products

Based on different experimental conditions for photocatalytic removal of VAN-B, varying formation of by-products was observed. Formation of organic by-products was determined by the increase in UV<sub>254</sub> that is caused by the rapid degradation of VAN-B during initial periods of treatment. Moreover, inorganic by-products formation (chloride and nitrate) continued during

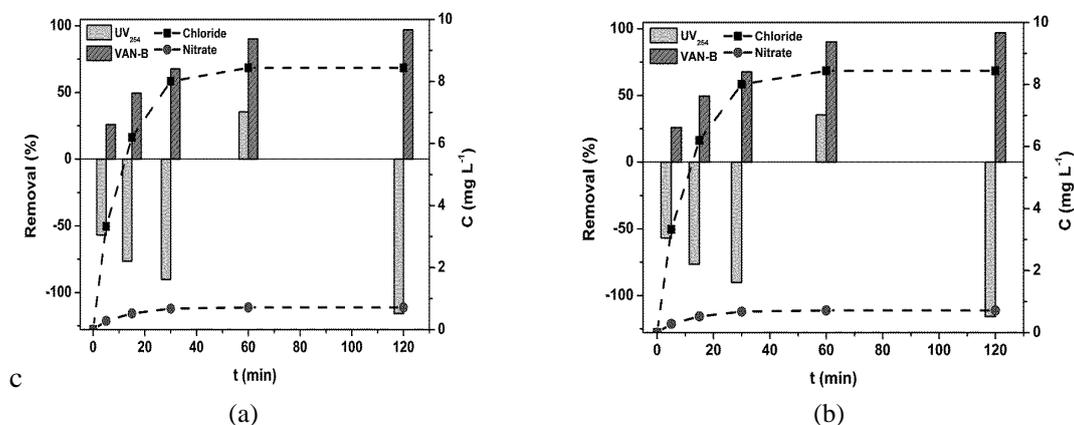


Fig. 6 Antibiotic removal and by-products formation ( $UV_{254}$ , chloride, nitrate) during photocatalytic oxidation of  $20 \text{ mg L}^{-1}$  VAN-B using (a)  $0.1$  and (b)  $0.5 \text{ g TiO}_2 \text{ L}^{-1}$  respectively

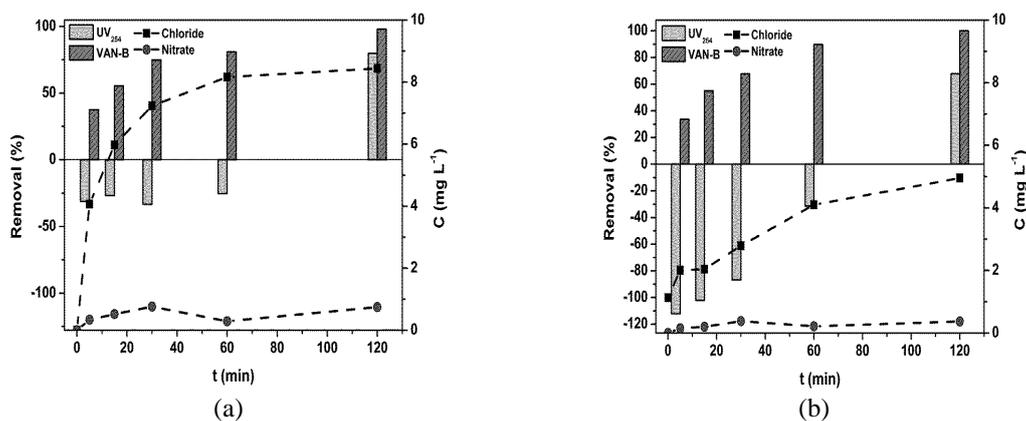


Fig. 7 Antibiotic removal and by-products formation ( $UV_{254}$ , chloride, nitrate) during photocatalytic oxidation of  $50 \text{ mg L}^{-1}$  VAN-B using (a)  $0.5 \text{ g TiO}_2 \text{ L}^{-1}$  and (b)  $0.5 \text{ g ZnO L}^{-1}$  respectively

oxidation process (120 min). As seen in Figs. 6 and 7, formation of by-products varied versus VAN-B concentration, type and concentration of each catalyst. These results are in accordance with previous findings by Lofrano *et al.* (2014).

Low *et al.* (1991) reported that formation of acetate can be associated with existence of carboxylic acid ( $\text{COOH-R}$ ) in VAN-B structure with  $pK_a$  value of 2.9. Thus ZnO performed better in terms of chemical group's oxidation as point of zero charge of ZnO is high to attract adsorption of it that resulted in a rapid degradation of VAN-B (Dimitrakopoulou *et al.* 2012) and consequently more toxic effluents as seen in Fig. 8.

### 3.8 Ecotoxicity evolution

The residual toxicity of treated VAN-B solutions ( $20 \text{ mg L}^{-1}$  and  $50 \text{ mg L}^{-1}$ ) is summarized in Fig. 8. The results of 24h and 48h immobilization test with *D. magna* are displayed in Figures 8a-b and Figs. 8(c) and 8(d), for the samples treated with  $\text{TiO}_2$  and ZnO respectively. The photo-decomposition of VAN-B is a complicated process with many intermediates that are of great

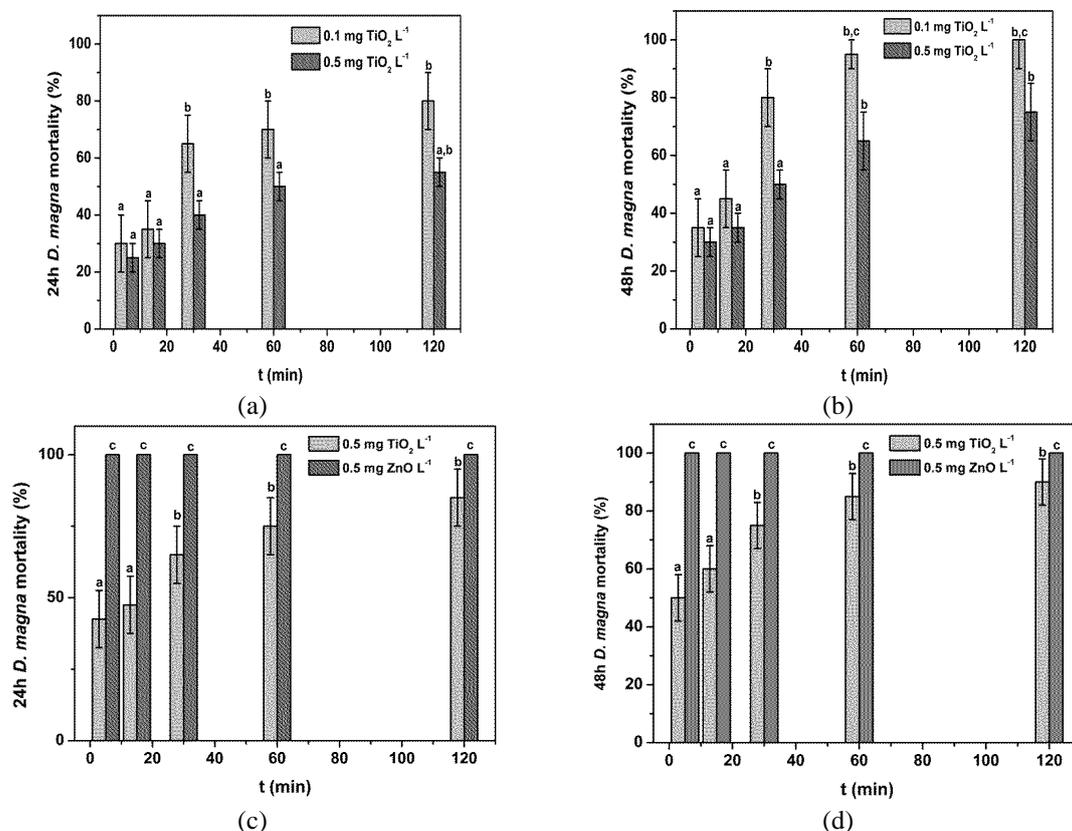


Fig. 8 Toxicity evolution during photocatalytic removal of (a) and (b) VAN-B ( $20 \text{ mg L}^{-1}$ ) using  $0.1$  and  $0.5 \text{ g TiO}_2 \text{ L}^{-1}$  at 24h and 48h, (c) and (d) VAN-B ( $50 \text{ mg L}^{-1}$ ) using  $0.5 \text{ g TiO}_2 \text{ L}^{-1}$  and  $0.5 \text{ g ZnO L}^{-1}$  catalysts at 24h and 48h

significance in water treatment because they can result in more toxic than the parent compounds (Bernabeu *et al.* 2011, Fatta Kassinos *et al.* 2011, Lofrano *et al.* 2014, Lofrano *et al.* 2016). As shown in Fig. 8(a), the excessive formation of transformation by-products due to increased radical oxygen species (ROS) production at higher  $\text{TiO}_2$  conditions (Fatta Kassinos 2011), resulted in different toxicity behaviour. Nevertheless, the toxicity of  $20 \text{ mg L}^{-1}$  VAN-B solution treated with  $0.5 \text{ g TiO}_2 \text{ L}^{-1}$  resulted no statistically different ( $p < 0.05$ ) after 5, 15, 30, 60 and 120 min of photo-oxidation (Fig. 8(a)). It worth to observe how increasing the test duration of 24h (Fig. 8(b)), the mortality effects significantly increased at both ( $0.1$  and  $0.5 \text{ g TiO}_2 \text{ L}^{-1}$ ) catalyst concentrations. Moreover, after 48h, an increasing trend in the amount of the residual toxicity at increasing with times of photo-oxidation could be observed.

Toxicity results of photocatalytic treated effluent *versus* time were in accordance with the VAN-B degradation kinetics and increasing formation of chlorides and nitrates. The relatively higher degradation rates compared to mineralization rates are inevitable promoters of by-products formation that caused toxicity in the effluent during whole period of photocatalytic process (Lofrano *et al.* 2014). The samples treated with  $0.5 \text{ g ZnO L}^{-1}$  resulted more toxic (a residual toxic effect up to 100% immobilization) compared to the samples treated with the same concentration of  $\text{TiO}_2$  (Fig. 8(c) and 8(d)).

#### 4. Conclusions

The present work is carried out to study the spatio temporal estimation of air quality parameters using LGP. The data consists of eight months measured concentrations of air pollutants from five monitoring stations. Spatio temporal models are developed considering the pollutants recorded at the neighbouring stations, atmospheric interactions between satellite cities and the prevailing wind direction.

From all the models, it can be seen that LGP could map the variations in the observed air quality. In general models achieved acceptable statistical measures in terms of band error. In most of the cases wind and distance based models are proved to be superior to other models as they consider the physics behind pollution dispersion. In this manner, the study of movements of pollutants over urban areas can help us understand their impact on pollution planning. Furthermore in depth study is necessary with respect to variation in wind direction, mixing height and pollution dispersion in spatio temporal modelling.

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