DOI: http://doi.org/10.21698/simi.2017.0003

INFLUENCE OF TiO_2 DOPANT TYPE UPON CYCLOPHOSPHAMIDE DEGRADATION EFFICIENCY

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Abstract

The influence of various dopant types like S, Fe, Co, Ni (5% wt.) in the photocatalytic degradation of cyclophosphamide under UV-VIS irradiation was investigated. The working conditions were as follows: irradiation time up to 270 minutes, photo catalyst dose 100 mg/L, initial pollutant concentration 19.15 mg/L. Pollutant degradation was found to follow a pseudo first order kinetic. CP degradation rate constants decreases in the following order $k_{Fe\text{-}TiO2} > k_{Ni\text{-}TiO2} > k_{Co\text{-}TiO2} > k_{S\text{-}TiO2} > k_{TiO2}$, which was also in accordance with chlorine mineralization rate constants.

Keywords: *advanced oxidation process, cyclophosphamide, metal and non-metal doped* TiO_2*, photo catalysis*

Introduction

Pharmaceutical compounds ussualy present a complex structure and can not be properly treated using conventional wastewater treatment processes (Zhang et al. 2013; Tiron et al. 2015). Cytostatics drugs residues were found in hospital wastewater discharges in concentrations up to μg/L (Mahnik et al. 2007; Kovalova et al. 2009; Mullot et al. 2009). Moreover just a part of administered cytostatic drugs are metabolized within human body (Zhang et al. 2013) and are presenting a potential danger upon human health and environment due to their cytotoxicity, genotoxicity, mutagenicity and teratogenicity (Constantin et al. 2016).

Cyclophosphamide (CP) is one of the most commonly cytostatic drugs to be found in sewerage systems. CP removal efficiency is largely dependent on wastewater treatment plant's operating parameters (Seira et al. 2016). Since conventional treatment processes are not assuring advanced degradation of CP there is a need for more performant treatment processes such as advanced oxidation processes (AOPs).

Among AOPs photocatalytic water treatment using TiO_2 is a well-known process used for wastewater treatment. TiO_2 assisted photocatalyse can mineralize a wide range of organic compounds (Nitoi et al. 2016) into harmless end products such as carbon dioxide, water, and inorganic ions.

TiO_2 doping with metals or non-metals can reduce the band gap of the doped catalyst, enabling light absorption in the visible region (Lazar et al. 2012) and therefore improving degradation efficiency. By doping TiO_2 more $\bullet OH$ and $\bullet O_2^-$ radicals are generated (Iliev et al. 2010). For example TiO_2 doped with Fe^{3+} presented an improved photocatalytic activity compared with un-doped TiO_2. Fe^{3+} can be easily inserted within TiO_2 structure due to the fact that Fe^{3+} and Ti^{4+} presents similar ionic radius (Farhangi et al. 2011; Crisan et al. 2016; Crisan et al. 2015).

The aim of the study was to investigate the influence of various dopant types: S, Fe, Co, Ni upon the photocatalytic degradation efficiency of cyclophospamide under UV-VIS irradiation.

Experimental

Photocatalytic experiments were performed using an UV Heraeus reactor with TQ150-Z1 immersed medium pressure mercury lamp. Aerobic conditions were assured through air bubbling Q = 50 L/h in order to avoid hole-electron recombination processes that are negatively influencing photocatalytic degradation efficiency.

The following reagents were used: cyclophosphamide (CP) (Sigma-Aldrich), TiO_2, 5%wt.S-TiO_2, 5%wt.Fe-TiO_2, 5%wt. Co-TiO_2, 5%wt.Ni-TiO_2 (synthesized by “Ilie Murgulescu” Institute of Physical Chemistry, Romanian Academy, via sol-gel method).

Determination of CP concentration was done by gas chromatography method using and Agilent 7890A gas chromatograph coupled with an Agilent 240 Ion Trap Mass Detector.

Chlorine mineralization was monitored using a Dionex ICS-3000 Dual Pump ion chromatograph.

Photocatalytic degradation were duplicated in order to assure reproducibility.

Results and Discussion

For an initial cyclophosphamide concentration $[CP]_0 = 19.15$ mg/L = 7.34×10^{-5} M irradiation time was varied within the domain 30-270 minutes. Photocatalyst dose was maintained at 100 mg/L.

The obtained degradation efficiencies are presented in Table 1.

Table 1. CP degradation efficiencies

Photocatalyst	TiO_2	S-TiO_2	Co-TiO_2	Ni-TiO_2	Fe-TiO_2
Time, min			η_{CP} ,%		
30	17.02	22.09	31.80	35.09	35.25
90	54.73	60.84	69.45	69.56	71.91
150	72.01	82.09	84.28	84.54	86.42
270	93.42	96.34	96.45	97.08	97.96

$[CP]_0 = 19.15$ mg/L = 7.34×10^{-5} M, [Photocatalyst] = 100 mg/L

Degradation efficiencies after 270 min of irradiation were higher than 93 % (for all catalyst types), residual CP concentration varying between 4.83×10^{-6} M (for un-doped TiO_2) and 1.49×10^{-6} M (for 5%wt.Fe-TiO_2).

Kinetic curves for all catalyst types were linearized by a pseudo-first order kinetic using the following equation.

$$[CP] = [CP]_0 e^{-kt} \tag{1}$$

$$-\ln(\frac{[CP]}{[CP]0} = k\ t \tag{2}$$

where k – pseudo-first order degradation rate constant, t – irradiation time, [CP] – cyclophosphamide concentration, $[CP]_0$ – initial cyclophosphamide concentration.

Rate constants k were calculated from the linear regression of equation 2. The linear regressions for all catalyst types are presented in Fig. 1.

Apart for using linearization method a non-linear least squares fit applied to equation 1 was used to calculate the constant rates and results for both linear and non-linear methods are presented within Table 2.

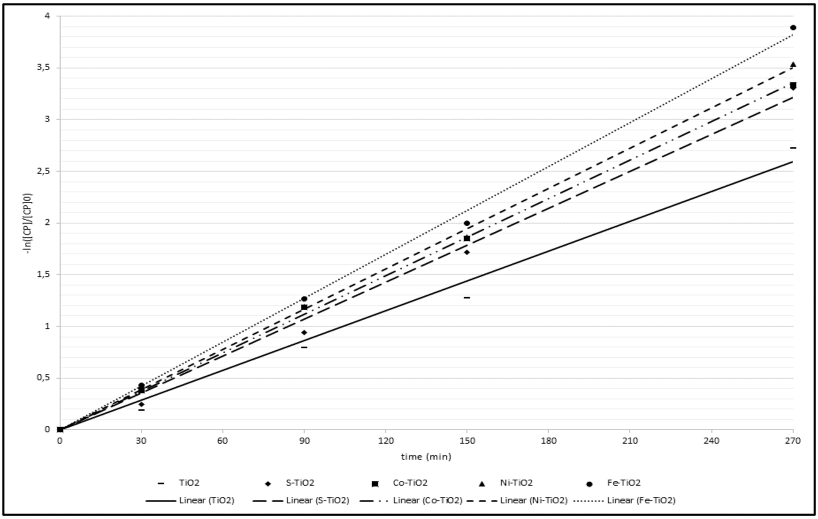

Figure 1. Linearization of CP degradation kinetic equations

Table 2. CP degradation rate constants
Linear *vs.* Nonlinear

Photocatalyst type	Linear		Nonlinear	
	R^2 (coefficient of determination)	k x 10^3 , min^{-1}	SS (sum of squares)	k x 10^3 , min^{-1}
TiO_2	0.9874	9.6	2.36 x 10^{-11}	8.54
S- TiO_2	0.9940	11.9	2.03 x 10^{-11}	10.52
Co- TiO_2	0.9993	12.4	1.25 x 10^{-11}	12.83
Ni- TiO_2	0.9988	13.0	4.42 x 10^{-12}	13.31
Fe- TiO_2	0.9977	14.2	1.54 x 10^{-12}	14.03

Pollutant degradation was found to obey pseudo first order kinetic. Degradation rate constants decreases in the following order $k_{Fe-TiO2} > k_{Ni-TiO2} > k_{Co-TiO2} > k_{S-TiO2} > k_{TiO2}$, which was also supported by chlorine mineralization efficiencies, presented in table 3, which were always lower that CP degradation efficiencies, due to formation of chlorinated intermediates.

Both linear and non-linear methods were also used in order to calculate organic chlorine mineralization rate constants. Linear equations are presented in Fig. 2 since a comparison between linear and nonlinear results is shown in Table 4.

Table 3. Chlorine mineralization efficiencies

Photocatalyst	TiO_2	S-TiO_2	Co-TiO_2	Ni-TiO_2	Fe-TiO_2
Time, min	η_{Cl} ,%				
30	16.70	21.88	27.64	28.99	31.10
90	34.17	38.58	49.53	55.86	57.78
150	44.92	55.48	65.65	67.57	74.29
270	71.60	84.65	88.49	92.72	94.64

$[CP]_0$ = 19.15 mg/L = 7.34 x 10^{-5} M, [Photocatalyst] = 100 mg/L

Table 4. Chlorine mineralization rate constants
Linear *vs.* Nonlinear

Photocatalyst type	Linear		Nonlinear	
	R^2 (coefficient of determination)	k x 10^3, min^{-1}	SS (sum of squares)	k x 10^3, min^{-1}
TiO_2	0.9889	4.5	0.098	4.46
S- TiO_2	0.9747	6.5	0.200	5.97
Co- TiO_2	0.9922	7.8	0.157	7.77
Ni- TiO_2	0.9787	9.2	0.194	8.80
Fe- TiO_2	0.9878	10.4	0.114	9.90

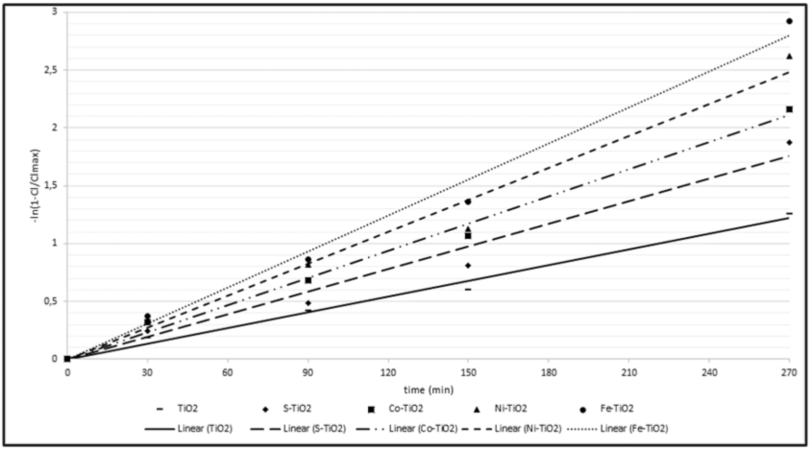

Figure 2. Linearization of Chlorine mineralization kinetic equations

Conclusions

CP degradation efficiencies were higher in the case of doped TiO_2 compared with un-doped TiO_2. The most efficient catalyst proved to be 5%wt.Fe-TiO_2 which assures a CP degradation efficiency higher than 97%, an organic chlorine mineralization efficiency higher than 94% and a remanent pollutant concentration of 1.49 x 10^{-6} M.
Constant rates for CP degradation and chlorine mineralization were calculated using both linear and non-linear models. Obtained values via linear method were compared with those calculated using a non-linear squares fit method and the results were

comparable, revealing the fact that CP degradation and chlorine mineralization processes are obeying a pseudo first order kinetic.

CP degradation rate constants followed the order $k_{Fe-TiO2} > k_{Ni-TiO2} > k_{Co-TiO2} > k_{S-TiO2} > k_{TiO2}$, which was also supported by organic chlorine mineralization rate constants.

Acknowledgements

The authors express their thanks for the un-doped TiO_2 and doped TiO_2 photocatalysts samples kindly provided by "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy.

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