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Research Article

Experimental Photodegradation of OPs and CBs by Advanced Oxidation Techniques in the Aqueous TiO2 Suspensions

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Abstract – The reaction of pesticides with the OH radical, is the most dominant annihilation reaction of the atmosphere. Phosmet, Azamethiphos, Coumaphos and Temephos were used as organophosphorous pesticides, and Methiocarb, Carbofuran and Pirimicarb compounds were used as carbamate pesticides with the aim of investigating the kinetics of the reactions of Organophosphorous (OPs) and Carbamate (CBs) Pesticides with the OH radicals. In aqueous TiO_2 suspensions, the degradation reactions via photocatalytic-effect of the seven pesticides selected as pollutants were analysed, and the impact of the initial concentration was calculated. All experiments were conducted in the same photoreactor and under the same conditions as three repetitions. The optimum amount of photocatalyst for the studied pesticide was determined and TiO_2 concentration for all experiments were taken as 0.2 g/100 mL. Considering that organic pollutants are present in water in trace amount, the initial concentrations for all organic compounds were added so as to be$1.0x10^{-4}$ molxL^{-1}, into the suspensions and the solution containing the organic pollutant. In this study, degradation speed of pesticides were determined experimentally, and the fastest degrading pesticide was tried to be found out.

Keywords – OPs, CBs, Photodegradation, TiO_2, Pesticides

I. INTRODUCTION

The harmful effect of organic pollutant on human health is becoming gradually severe with the development of industry and agriculture [1]-[2]. Due to their stable chemical structure, these pollutants are resistant to biological and photocatalytic degradation; thus alternative and effective treatment process for them is essential. Recently, it has been witnessed that innovative technologies have been developed, and advanced oxidation processes have been used to remove organic residues. Basically, photocatalytic processes, using semiconductors, which can generate reactive OH radicals when exposed to UV-radiation were analysed in detail [3]-[4].

Photocatalytic oxidation is one of the advanced technologies used for the removal of pollutants due to the mineralization activities of organic pollutants. In an ideal condition, this process generates carbondioxide, water, and inorganic mineral ions [5]. Among photocatalysts, TiO_2, which is a semiconductor, is the most commonly used, because it can be obtainable, it is cheap, is not toxic and has a relatively high chemical stability [6]. TiO_2 was used successfully for the degradation fragmentation of the pesticides [7]-[9].

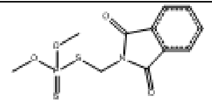
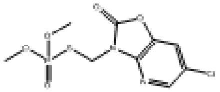
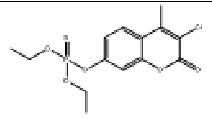
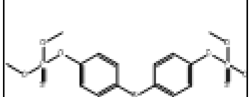
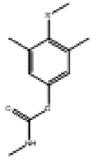
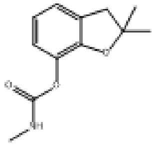
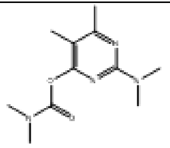
It has been observed that energy is generated when semiconductive suspensions are illuminated, and OH radical comes out as an intermediate product. Extremely oxidizing particles occur in an environment with TiO_2. It is not necessary to use pricy chemical substances in order to implement oxidation reactions. The UV radiation of sunlight can start these reactions and the oxygen in the air is sufficient for the oxidation reaction to come into effect. The negative part of this method is the use of a water-insoluble photocatalysts. In the end of the process the semiconductive suspension should be removed from the water, and should be sent back to the system for each process [9]-[11].

The organophosphorous pesticides, which started to be used after World War II, comprise 45% of the pesticides worldwide. Being easily synthesized has led to the diversification of organophosphorus compounds. The physicochemical properties such as evaporation of active substances, solubility in water, toxicity differ significantly. Therefore, an appropriate organophosphorous active substance can be found for almost each pest. The organophosphorous pesticides can be effective though skin, digestion, or respiration [12]. The effect mechanism and permanence of the OPs is usually dependent on the property of the chemical structure binding to the phosphorus atom. As a chemical structure, OPs are esters of phosphorous acid. Usually, two ester groups, methoxy or ethoxy are attached to the phosphorous atom. The third ester group may be aliphatic, homocyclic, or heterocyclic structures, and are attached to the ester atom by an ester or thioester bond. This weak bond increases the electrophilic property of the phosphorous atom, and gives it an electron affinity property. OPs are majorly affected by chemical reactions such as hydrolysis and oxidation. Those with P=0 properties can be hydrolysed easier and their persistency is therefore lower when compared to those with P=S properties, However, the ones with P=0 have a higher water-solubility [13].

Carbamate compounds, which are carbamine acid esters, are insecticides and comprise a smaller class when compared to organophosphorous insecticides. They are formed by the replacement of a carboxyl onto the amine radical instead of the hydrogen atom. The CBs have high polarity, water-solubility and thermal non-stability properties. Due to their acute toxic effect, they are poisonous (toxic) for living organisms [14]. In addition to oxidation, biotransformation, hydrolysis, biological growth, photolysis, and biodegradation, CBs can transform into many products through various ways such as reactions with living organisms [15]. In addition to the ability to metabolise the CBs, the microbial populations in the soil can also adapt themselves against many metabolites of the CBs. These pesticides and their metabolites may affect the microflora and soil fertility. Although CBs are very stable in aqueous environments, the application of these toxic compounds may lead to a significant decrease in non-targeted organisms [16].

Two-dimension figures, molecule names (the acronyms used), the formula of the molecules of the seven pesticides used in this study are given in Table 1. OP1, OP3 and OP4 molecules, with their P=S bond, are classified in the thiophosphates group, and only OP1, with its 2S and 2O atom, is named as dithiophosphate. Although the OP2 molecule has a P=O bond, it is classified within thiophosphate group due to the 1S and 3O atoms in its structure. The R groups of all OPs are different. While OP1 and OP2 have 2 tips of methoxy for each, OP3 has two ethoxy tips, and OP4 has two symmetrical methoxy tips for each. Moreover, when CBs are analysed, it is determined that the R groups, which are bound to the carboxyl group in three of the molecules are different. While there is one methyl group on the tip bound to N in CB1 and CB2, there are two methyl groups bound to N in CB3 molecule.

Table 1. Two-dimensional figures, molecule names (the acronyms to be used) and molecule formulas

Two-dimensional Figures of the Molecules	Molecule Names	Molecule Formulas
	(OP1) Phosmet	$C_{11}H_{12}NO_4PS_2$
	(OP2) Azamethiphos	$C_9H_{10}ClN_2O_5PS$
	(OP3) Coumaphos	$C_{14}H_{16}ClO_5PS$
	(OP4) Temephos	$C_{16}H_{20}O_6P_2S_3$
	(CB1) Methiocarb	$C_{11}H_{15}NO_2S$
	(CB2) Carbofuran	$C_{12}H_{15}NO_3$
	(CB3) Pirimicarb	$C_{11}H_{18}N_4O_2$

II. MATERIALS AND METHOD

In the experiment, stock solutions of the pesticides used were prepared in an amount of $1.0x10^{-2}$ molxL^{-1}. In order to prepare the reaction solution, the determined amount of TiO_2 was calculated and put into the reaction vessel, and distilled water was added onto it in order to prepare the suspension. The reaction vessel was shaken in the ultrasonic bath for 15 minutes so as to prepare a good suspension. Organic pollutant concentration was set to be $1.0x10^{-4}$ molxL^{-1} by adding the stock solution into this suspension, and the volume of the suspension was completed to be 600 mL. Samples of 10 mL were taken from the prepared suspension, and the rest was placed into the photoreactor in order to be irradiated. Since the normal filtration was not sufficient, the samples were filtered in vacuum using 0,2 μm filter papers in order to remove the TiO_2 particles from the environment. The filtrates were taken into test tubes, and the absorbance of the samples at λmax = 318 nm value was read using UV-visible spectrophotometer (Perkin Elmer), and their concentration was determined with the help of calibration graphics. The pesticides and TiO_2, which were used in the experiments, were provided from Sigma-Aldrich. The experiments were conducted using a special cylindrical Keriman UV18/8 brand photoreactor, the shape of which is given as top view in Figure 1.a, and as side view in Figure 1.b. As seen in Figure 1.c, the internal part of the cylinder has equally spaced 18 UV fluorescent lamps of 8W as a light source. In all experiments, The beaker, which was used in all experiments as a reaction vessel was shaken in order to provide a homogenous distribution of TiO_2 particles in the suspension.

a b c

Figure 1. The Photoreactor System

III. RESULTS

A. The Impact of the Photocatalyst Concentration

In order to determine the impact of the photocatalyst, the TiO2 concentration was changed so as to be (0.1- 0.5) g/100 mL, the initial concentration of which was 1.0x10-4 molxL-1 at its natural pH in all suspensions. The results obtained are given in Figure 2; being degradation % at 30, 60, and 90 minute-periods respectively at y-axis, and (0.1- 0.5) g/100 mL of TiO_2 values at x-axis. As the TiO_2 concentration increases, photocatalytic degradation speed increases up to a certain limit concentration of TiO_2, and then it reveals a slow decrease. It was found out that the maximum degradation was at 0.2 g/100 mL of the TiO_2 concentration, and this was taken as optimum photocatalyst concentration in all testings.

After the 0.2 g/100 mL optimum value in Figure 2, it was determined that other factors got involved affecting the degradation reaction speed. As the TiO_2 concentration in the system increases, the interparticle distance decreases. Particles form clusters by coming together, and this leads to the interphase surface to reduce. Since organic matters are oxidised on TiO_2 surface by their .OH, the reduction of the interphase surface reduces the possibility of the oxidation of substances; in other words, it reduces the possibility of fragmentation into smaller substances. Moreover, TiO_2 particles prevent the system from absorbing light, and even lead to light scattering.

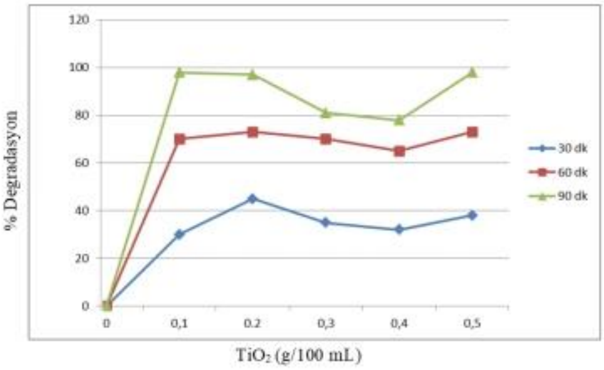
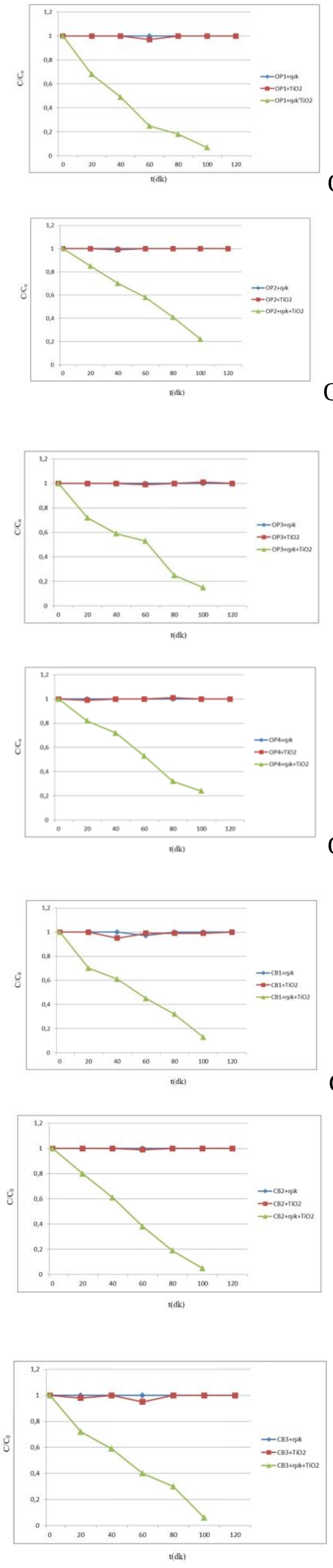


Figure 2. Optimum Photocatalytic Degradation

B. The Impact of Light and Photocatalyst

In order to conduct the degradation of organic matters in heterogeneous photocatalytic degradation systems, the three factors, namely light-semiconductor-O_2, have to be altogether present in the system. Pretestings were conducted in order to determine the impact of light alone on the degradation of substances, and the absorption on TiO_2 particle surface for each substance. These experimentations were carried out for each substance individually under three conditions, which were in the presence of light only, in TiO_2 presence only, and in the presence of TiO_2+light. The results of these experimentations are shown in Figure 3 for each substance respectively. The figures reveal the change of C/Co against time (t). Co is taken as the initial concentration of the substance, whereas C shows the concentration of the substance in t time.



OP1

OP2

OP3

OP4

CB1

CB2

CB3

Figure 3. Light and TiO_2 impact of OP1-CB3 on Photocatalytic Degradation

C.The Impact of the Initial Concentration

The impact of the inital concentration on photocatalytic degradation speed was analysed by changing the initial concentration for all substances as (6.0-14.0).10^{-5} mol/L. The k rate constants, and r regression values are given in Table 2,3. The reaction rate constant decreases as the initial concentration increases. However, this decrease declines at lower concentrations.

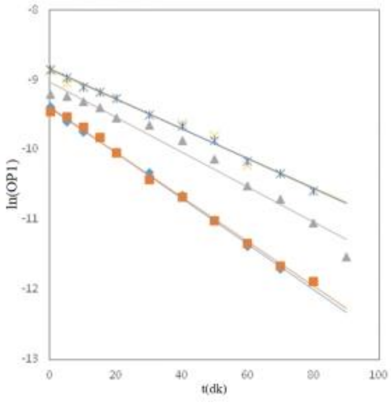
Table 2. The Impact of Initial Concentration

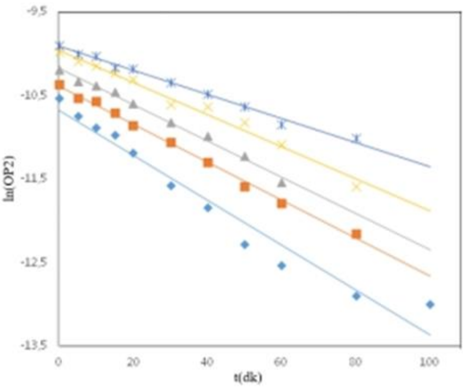
	6.0x10^{-5}	**8.0 x10^{-5}**	**10.0 x10^{-5}**
OP1			
k /10^{-18} min^{-1}	2,45±0,002	2,13±0,003	**1,76±0,001**
r	0,9885	0,9748	**0,9526**
OP2			
k / 10^{-14} min^{-1}	2,28±0,002	3,78±0,004	**5,36±0,003**
r	0,9822	0,9623	**0,9934**
OP3			
k /10^{-11} min^{-1}	5,16±0,005	6,23±0,002	**8,69±0,001**
r	0,9771	0,9911	**0,9847**
OP4			
k /10^{-9} min^{-1}	6,98±0,003	7,66±0,004	**9,55±0,006**
r	0,9863	0,9754	**0,9962**
CB1			
k /10^{-7} min^{-1}	5,87±0,001	8,65±0,004	**10,35±0,002**
r	0,9998	0,9885	**0,9874**
CB2			
k / 10^{-8} min^{-1}	6,46±0,001	7,21±0,005	**8,23±0,002**
r	0,9711	0,97626	**0,9811**
CB3			
k /10^{-12} min^{-1}	4,27±0,007	5,36±0,001	**6,79±0,004**
r	0,9624	0,9832	**0,9974**

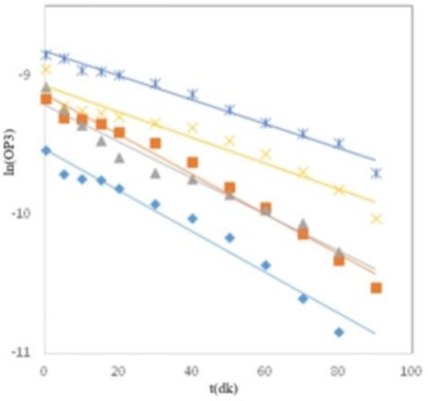
Table 3. The Impact of Initial Concentration

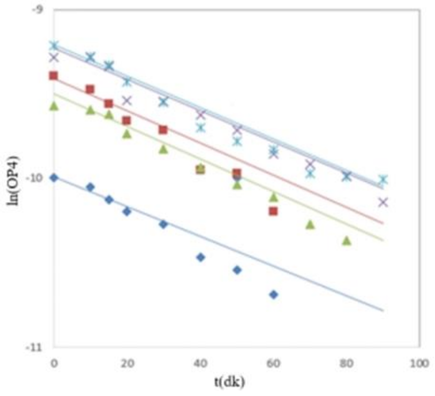
	12.0 x10^{-5}	**14.0 x10^{-5}**
OP1		
k /10^{-18} min^{-1}	1,58±0,004	0,99±0,005
r	0,996	0,9874
OP2		
k / 10^{-14} min^{-1}	4,45±0,001	3,99±0,002
r	0,9725	0,9855
OP3		
k /10^{-11} min^{-1}	7,21±0,006	6,77±0,005
r	0,9689	0,9632
OP4		
k /10^{-9} min^{-1}	8,46±0,007	7,01±0,001
r	0,9977	0,9947
CB1		
k /10^{-7} min^{-1}	9,11±0,005	7,24±0,007
r	0,9966	0,9921
CB2		
k / 10^{-8} min^{-1}	6,15±0,002	5,87±0,001
r	0,9962	0,9744
CB3		
k /10^{-12} min^{-1}	6,02±0,001	5,49±0,003
r	0,9724	0,9855

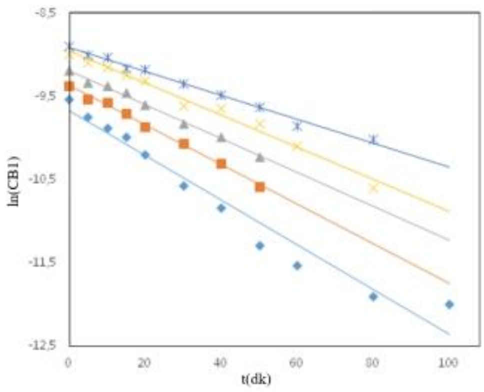
The experimentation results are given in Figure 4 respectively. The figures show the e-base logarithm, and the change of lnC according to time for different initial concentrations of organic matter concentrations. As it can be seen in the figures, reaction rate constant declines while the initial concentration increases. However, this decline decreases at lower concentrations.

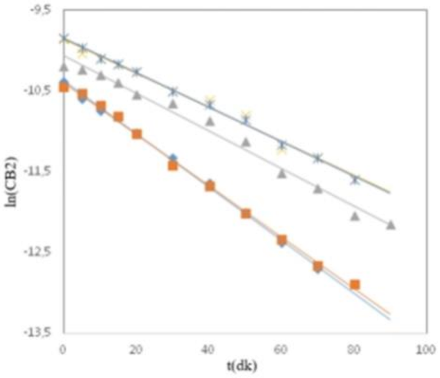


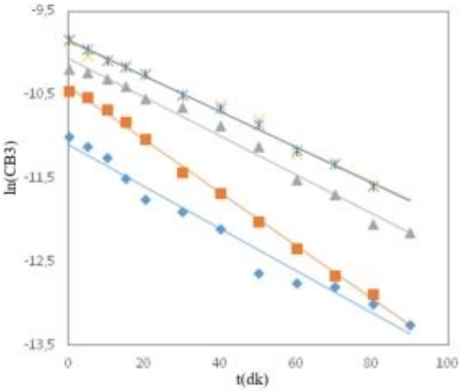












¨ 6x10^{-5} molxL^{-1} ■ 8x10^{-5} molxL^{-1} ▲ 10x10^{-5} molxL^{-1} X
12x10^{-5} molxL^{-1} ✱ 14x10^{-5} molxL^{-1}

Figure 4. The Impact of the Initial Concentration of OP1-CB3 on Photocatalytic Degradation Rate

IV. DISCUSSION

In order to determine the effect of photocatalyst concentration, TiO_2 concentration was changed as 0.1-0.5 g/100 mL in suspensions with initial concentrations of 1.0.10^{-4} mol.L^{-1} at the natural pH of all substances. As the TiO_2 concentration increases, the photocatalytic degradation rate increases up to a certain limit concentration of TiO_2, and then a slow decrease is observed. The maximum degradation was obtained when the TiO_2 concentration was 0.2 g/100 mL, and this concentration was accepted as the optimum photocatalyst concentration in all experiments. These results show that after the optimum value, other factors that affect the rates of degradation reactions of pollutants come into play. As the TiO_2 concentration in the system increases, the distances between the particles decrease. Particles come together to form clusters.This results in a shrinkage of the interphase surface. Since the organic substances on the TiO_2 surface are oxidized by OH radicals, the shrinkage of the interphase surface reduces the oxidation of these substances, that is, the possibility of decomposition into smaller substances. In addition, TiO_2 particles prevent the system from absorbing light and even cause light to scatter.

As a result of this study, there was no concentration change in the studied substances when they were only illuminated. When the studied substances were kept in the dark in the presence of TiO_2, there was a concentration change of 1-3% due to absorption. In an environment with both light and TiO_2 at the same time, it was determined that there was a degradation to a great extent in all the substances. By the end of 100 minutes, the concentration change was calculated as 93% for OP1, 78% for OP2, 85% for OP3, 76% for OP4, 87% for CB1, 95% for CB2, and 94% for CB3. Based on these results, it was determined that the most degraded pesticide among organophosphorous pesticides was OP1, while CB2 was the one among carbamate pesticides.

As the initial concentration of the studied substances is increased, the rate constant decreases. However, the decline decreases at low concentrations. Due to the rate constant k being dependent on the initial concentration, it can be said that the degradation reaction occurs apparently as a first order reaction. One of the phases is $\cdot OH$ radicals while the other phase is OH^- ions absorbed at TiO_2 surface. Since the studied substances are also aimed to be absorbed at TiO_2 surface, it inconveniences the transition of OH^- ions into the catalytic spaces at the surface, thus decelerates the formation of OH radicals. According to the k rate constant values, the fastest among organophosphorous pesticides is found out to be OP4, whereas the one among carbamate pesticides is determined as CB3, since both of these molecules have higher k value within their group, and react faster than the others. Overlaps were observed for $6x10^{-5}$ and $8x10^{-5}$, and for $12x10^{-5}$ and $14x10^{-5}$ $molxL^{-1}$ initial concentrations of OP1 given in Figure 3. The reason is thought to be the impact of the functional groups, which are bound to the molecule. There is a similar situation for CB2. However, in OP4 molecule, there was an overlap found out at $12x10^{-5}$ and $14x10^{-5}$ $molxL^{-1}$ initial concentrations, and the reason was thought to be due to the symmetry of the molecule.

V. CONCLUSION

Theoretical studies were also carried out for all molecules studied. Theoretical work has been published for six molecules other than Phosmet [17] Experimental and theoretical results have been published for Phosmet (OP1), one of the seven pesticides studied [13]. When the theoretical results in these two published articles and the experimental results in this study are examined:

At the theoretical stage, the molecule that will enter the reaction most voluntarily, that is, the molecule that requires the lowest energy, is Temephos from organophosphorus pesticides and Methiocarb from the group of carbamate pesticides.

In the experimental study, when light and TiO_2 are present in the environment at the same time, all of the substances are degraded to a large extent and after 100 minutes, Phosmet with a concentration change of 93 % and carbofuran with a concentration change of 95 % are the pesticides that degrade the most. According to the k rate constant values, the fastest among organophosphorous pesticides is found out to be Temephos, whereas the one among carbamate pesticides is determined as Pirimicarb, since both of these molecules have higher k value within their group, and react faster than the others. In both experimental and theoretical results, it is a successful result that temephos is the fastest degrading molecule, that is, the fastest reacting molecule.

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REFERENCES

[1] R. Gioia, J. Dachs, L. Nizzetto, R. Lohmann, KC. Jones, "Atmospheric transport, cycling and dynamics of Polychlorinated Biphenyls (PCBs) from source regions to remote oceanic areas: occurrence, fate and impact of atmospheric pollutants on environmental and human health," *American Chemical Society*, Vol. 1149(16) , pp. 3-18 , 2013.

[2] K. Vorkamp, K. Bester, FF.Rigét, "Species-specific timetrends and enantiomer fractions of (HBCD) hexabromocyclododecane in biota from east Greenland," *Environ. Sci. Technol.*, Vol. 46, pp.10549-10555, 2012.

[3] I. Losito, A. Amorisco, F. Palmisano, “Determination of Ochratoxin A in green coffee beans by solid-phase microextraction and liquid chromatography with fluorescence detection,” *Journal of Chromatography A* Vol. 1187 (1-2), pp. 145-150, 2008.

[4] MA. Oturan, JJ. Aaron, “Advanced oxidation processes in water/wastewater treatment: principles and applications, A review,” *Crit. Rev. Environ. Sci. Technol*., Vol. 44, pp. 2577-2641, 2014.

[5] Y. Wang, H. Zhao, J. Gao, G. Zhao, Y. Zhang, “Rapid mineralization of azo-dye wastewater by microwave synergistic electro-fenton oxidation process.” *J. Phys. Chem. C*, Vol. 116, pp. 7457-7463, 2012.

[6] X. Chen, SS. Mao, “Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications,” Chem. Rev., Vol. 107, pp. 2891-2959, 2007.

[7] M. Sturini, E. Fasani, C. Prandi, A. Casaschi, A. Albini, “Titanium-dioxide photocataysed decompostion of some thicarbamates in water,” *J. Photochem, Photobiol. A: Chem.*Vol.101, pp. 251-255, 1996.

[8] HF. Lai, CC. Chen, RJ. Wu, CS. Lu, “Thiobencarb degradation by TiO_2 photocatalysis: parameter and reaction pathway investigations,” *J. Chin. Chem. Soc*., Vol. 59, pp. 87-97, 2012.

[9] Y. Yalçın Gürkan, E. Kasapbaşı, Z. Çınar, “Enhanced solar photocatalytic activity of TiO_2 by selenium.(IV) ion-doping:Characterization and DFT modeling of the surface,” *Chemical Engineering Journal,* Vol. 214, pp. 34-44, 2013.

[10] S. Dass and M. Munerr, KR. Gopidas, “Photocatalytic degradation of wastewater pollutants. Titanium-dioxide-mediated oxidation of polynuclear aromatic hydrocarbons,” *Journal of Photochemistry and Photobiology A: Chemistry,* Vol. 77 (1), pp. 83-88, 1994.

[11] RW. Matthews and SR. McEvoy, “Photocatalytic Degradation of Phenol in the Presence of Near-UV Illuminated Titanium Dioxide,” *Journal of Photochemistry and Photobiology A: Chemistry,* Vol. 64, pp. 231-246, 1992.

[12] K. Alejo González, E. Hanson Viana, R. Vazquez Duhalt, “Enzymatic detoxification of organophosphorus pesticides and related toxicants,” *J Pestic Sci.* Vol. 43(1), pp. 1–9, 2018.

[13] B. Eren, Y. Yalçın Gürkan, “Theoretical and experimental photodegradation of Phosmet via oxidation techniques in the presence of aqueous TiO2 suspension,” *Bulgarian Chemical Communications,* Vol. 53, pp. 456-463, 2021.

[14] A. Alvarez, JM. Saez, JSD. Costa, VL. Colin, MS. Fuentes, SA. Cuozzo, CS. Benimeli, MA. Polti., MJ. Amoroso, “Actinobacteria: Current research and perspectives for bioremediation of pesticides and heavy metals,” *Chemosphere*. Vol. 166, pp. 41-62, 2017.

[15] ZQ. Cai, J. Wang, JT. Ma, XL. Zhu., JY. Cai, GH. Yang, “Anaerobic Degradation Pathway of the Novel Chiral Insecticide Paichongding and Its Impact on Bacterial Communities in Soils,” *Journal of Agricultural and Food Chemistry*, Vol. 63, pp. 7151-7160, 2015.

[16] M. Gupta, S. Mathur, TK. Sharma, M. Rana, A. Gairola, NK. Navani, R. Pathania, “A study on metabolic prowess of Pseudomonas sp RPT 52 to degrade imidacloprid, endosulfan and coragen,” *Journal of Hazardous Materials*, Vol. 301, pp. 250-258, 2016.

[17] B. Eren, YY. Gürkan, “Possible reaction pathways of selected organophosphorus and carbamate pesticides according to the DFT calculation method,” *Bulgarian Chemical Communications,* Vol. 54 (3), pp. 224-234, 2022.