

UNCATALYZED PEROXOMONOSULPHATE DEGRADATION OF PARA AMINOPHENOL, A POTENTIAL POLLUTANT

MANILA, NEHA BHATT*, ANSHU PAL AND SANDHYA SHARMA

Department of Chemistry, Kanya Gurukul Campus, Gurukul Kangri Vishwavidyalaya, Haridwar

(Received 22 January, 2020; accepted 6 February, 2020)

ABSTRACT

The present work reports on degradation of para aminophenol (PAP) using potassium monopersulphate (PMS) as oxidizer without using any catalyst. All the factors affecting the degradation were studied. The kinetic and thermodynamic results showed that for the oxidation of 25 mL of reaction mixture in which concentration of PAP was 0.0001M, the optimal conditions were- volume of PMS = 5mL (0.01M), temperature = 32-38 °C and pH = 6.5-7.0. The UV and IR spectra of the results revealed the formation of benzoquinone as product.

KEY WORDS : Para aminophenol, Potassium monopersulphate, Degradation, Kinetic, thermodynamic, Oxidation, Optimal etc.

INTRODUCTION

The largest source producers of non-biodegradable pollution are pharmaceutical compounds and antibiotic residues, which affect the aquatic life (Kadji *et al.*, 2017; Aissani-Benissad *et al.*, 2016; Madi *et al.*, 2018; Aissani-Benissad *et al.*, 2013; Fourcade *et al.*, 2013). When concentration of these molecules ranges from 1-100 mg/L, which is comparatively much high than the detected concentration in the environment, acute toxicity is observed on aquatic and terrestrial organisms and wildlife (Amrane *et al.*, 2019). The concentration reported for pharmaceutical compounds is from nanogram/L to microgram/L. The concentration of paracetamol in sewage treatment plant effluents in Spain and Korea has been observed at 0.22 and 6.8 mg/L and in South Korea and France, it is at 0.33 and 0.071 mg/L (Agüera *et al.*, 2012; Aguilar *et al.*, 2012). Para aminophenol (PAP) is considered to be aniline's aromatic ring-hydroxylated metabolites. A vast research work has been focused on PAP, since it is a metabolite for acetaminophen, most widely used analgesic. Unfortunately, it damages the S3 segment of proximal tubule in kidney and is nephrotoxic. It is acutely nephrotoxic in rats, for example F344 rats, Long-Evans rats and Sprague-Dawley rats (Calder *et al.*, 1971; Green *et al.*, 1969). PAP is a major

component used in preparation of paracetamol, an analgesic and anti-pyretic drug, in pharmaceutical industries. Hundreds of tons each year is consumed by Scandinavian countries (Brorström Lundén *et al.*, 2009). According to the reports of Togola and Budzinski (2008), treated waste water effluents contain paracetamol as high as 200 mgL⁻¹. Due to its discharge to the environment, its concentration is highest compared to other pharmaceuticals (Cren-Olivé *et al.*, 2011). The residual paracetamol has adverse effects on aquatic life (Boxall, 2008). In order to oxidize paracetamol in aqueous solutions, advanced oxidation processes have applied. Methods like H₂O₂/UV (Andreozzi *et al.*, 2003), ozonation (Andreozzi *et al.*, 2003; Arias *et al.*, 2006), anodic oxidatives (Arias *et al.*, 2005), oxidation by photocatalyst (Ray *et al.*, 2009) etc. are the methods used for degrading paracetamol. Besides AOP techniques, pulsed corona discharge, a non thermal plasma method has a potential for degrading paracetamol (Hatakka *et al.*, 2013). To degrade recalcitrant organic pollutants AOPs again become more common way. The oxidants involve in these processes like oxygen, ozone and peroxides such as H₂O₂, HSO₅⁻ and S₂O₈²⁻, can completely degrade pollutants to harmless substances (Grübel *et al.*, 2017; Duan *et al.*, 2015). The use of sulphate radical for degradation of PAP or paracetamol gained a

growing attention. Generation of sulphate radicals by thermoactivated peroxydisulphate process having a longer lifetime (30-40 ms) than hydroxyl radical (10-3 ms) (Kadji *et al.*, 2017; Aissani-Benissad *et al.*, 2016; Mahvi *et al.*, 2015). The mentioned range of pH could be 3-8. Sulphate radicals have high selectivity (Quan *et al.*, 2010). In presence of electron withdrawing group, the electrophilicity of sulphate radicals is high [Carter, *et al.*, 2016; Crimi *et al.*, 2010]. Various methods have been used in which acetaminophen has removed by using sulphate radicals like Fe²⁺/CuO/PDS (Zhang, *et al.*, 2018), Fe₂O₃/Cu₂O/PDS (Hong *et al.*, 2017), Fe0/PDS (Lu *et al.*, 2019), bicarbonate/PDS (Feng *et al.*, 2018), Fe²⁺/PDS (Lu *et al.*, 2017), pyrite (FeS₂)/PDS (Deng *et al.*, 2014), etc.

Oxone is a very strong oxidizing agent and produces H₅O₅⁻ ions. In present work, we had investigated the oxidation of para aminophenol by potassium monopersulphate, salt of caro's acid without any use of catalyst. In this order, optimum conditions for degradation were tried to be found and the results are discussed and compared.

NOVELTY AND LIMITATIONS

Although various chemical and adsorptive methods have been used for removing the pollutant PAP, but it's kinetic study of removal by using oxone is not found in literature. Oxone readily oxidizes PAP into product benzoquinone. The process is un-catalysed. Furthermore, non-toxic and easily available chemicals were used for present work.

Although the present work is very rapid and accurate, but still it has some limitations, which are as follows-

- Maximum decomposition of PMS in phosphate buffered medium, favoured in either slightly acidic or neutral condition (Donald *et al.*, 1955) at 33.2 °C.
- The concentration of buffer must be high, since the product H₂O₄⁻ after decomposition of PMS, is much stronger acid than the reactant HSO₅⁻.
- Highly concentrated buffer maintains the constant pH of the reaction mixture.

The concentration of [PMS] must be at least 20 times higher than [PAP].

MATERIALS AND METHODS

Materials

The target compound: Para aminophenol (C₆H₇NO,

99% pure) was obtained from Alfa Aesar.

Other chemicals such as PMS (peroxomonosulphate) was Sigma Aldrich make. It was supplied in the form of triple salt 2KHSO₅·KHSO₄·K₂SO₄ (oxone). Potassium dihydrogen orthophosphate (KH₂PO₄), sodium hydroxide (NaOH), acetone and sodium chloride (NaCl) were obtained from Fischer Scientific. All of them were of AR grade. Triply distilled water was used during all the experiments. All the solutions were freshly prepared before use.

Apparatus

The spectra of the reaction mixture was obtained with UV-VIS spectrophotometer (SYSTRONICS-118). IR spectra of degradation of PAP was recorded on SHIMADZU FTIR-8400S within the wavelength range 4000-400 cm⁻¹ at room temperature. pH of the reaction mixture was maintained by using SYSTRONICS-Digital pH meter - 335.

Preparation of buffer

Potassium dihydrogen orthophosphate buffer of 0.5M strength having pH 4.0, was prepared in 100mL volumetric flask. 6.8045 g of KH₂PO₄ was dissolved in triply distilled water and made up to 100 mL in a volumetric flask. The pH of this buffer was maintained to be 7.0 by using sodium hydroxide solution, prepared by dissolving NaOH pellets in triply distilled water.

RESULTS AND DISCUSSION

Pathway of degradation of PAP: PAP degradation is shown in Fig. 1. Absorption spectra for the reaction mixture was recorded at different time intervals for 240 minutes in order to identify the intermediates. In absence of PAP i.e. when reaction mixture contained only peroxomonosulphate with phosphate buffer, comparatively weak absorption spectra was observed near by 200 nm as PAP was added, a red shift compared to PMS and buffer mixture, was observed which indicates the initiation of the formation of product. After proceeding reaction for 240 minutes, absorbance at this particular wavelength in visible range, i.e. 395nm, was increased sufficiently.

The IR spectra of degradation of PAP shows the disappearance of strong double peaks at 1500 cm⁻¹ confirmed the cleavage of the phenyl ring (Min *et al.*, 2007). Moreover, peaks at 3128.64, 1708.99, 1634 and 893.07 indicated C-H stretching of an alkene, C=O

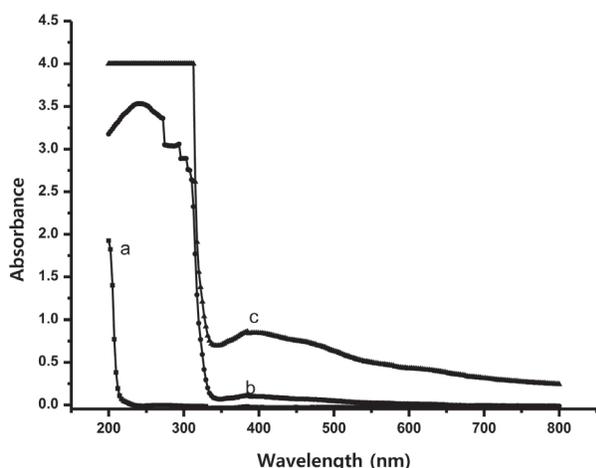


Fig. 1. UV-VIS absorption spectrum of uncatalyzed PAP degradation by PMS. (a) Absorption spectrum of [PMS] + phosphate buffer, (b) absorption spectrum of [PAP] + [PMS] + phosphate buffer on initiation of the reaction, (c) absorption spectrum of [PAP] + [PMS] + phosphate buffer after 4 hours of the initiation of the reaction.

stretching for cyclohexanone, C=C stretching for disubstituted cis form and C-H bending for 1,2-disubstituted carbons. This data resembles with the structure of the major product benzoquinone.

Order with respect to PAP and PMS: The effects of all parameters were carried out with $[PAP] < [PMS]$, except for the determination of order with respect to substrate, i.e. PAP. For these conditions, the orders with respect to PMS and PAP were found to be fractional as ≈ 1.5 and 0.8 . The slope of $\log k_{obs}$ and $\log [PMS]$ gave the order with respect to [PMS], shown in Fig. 2, while slope of $\log k_{obs}$ and $\log [PAP]$ gave the order with respect to PAP, shown in Fig. 3.

In the present study, in aqueous acidic medium, PMS exists probably as HSO_5^- ion. Since PMS and PAP are having fractional order, hence a complex may form between them which readily converted to product benzoquinone and some other by products. It was observed that [PAP] had a negative effect, whereas [PMS] had a positive effect on the yield of degradation of PAP. Since the sulphate radicals ($SO_4^{\cdot-}$) generated after decomposition of PMS in phosphate buffer, are very reactive species, hence their accumulation in the medium do not take place. So, a stationary state was attributed for these radicals, due to which a pseudo fractional order kinetics was assumed. Hence these results form the basis of our further study for working out various results with varying concentrations and conditions of the reaction under study.

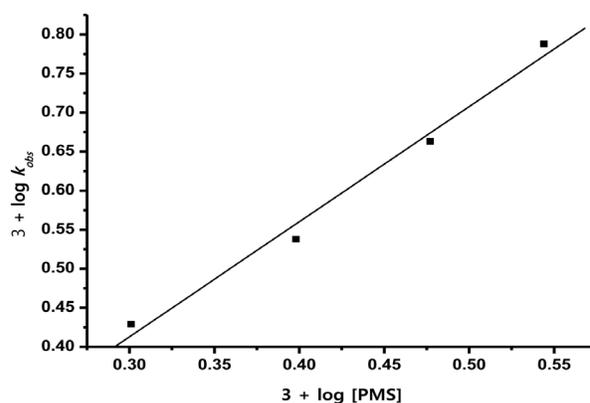


Fig. 2. Plot of $\log k_{obs}$ versus $\log [PMS]$ $[PAP] \times 10^4 = 1$ M, $pH = 7.0$, $T = 32^\circ C$, $\lambda_{max} = 395nm$

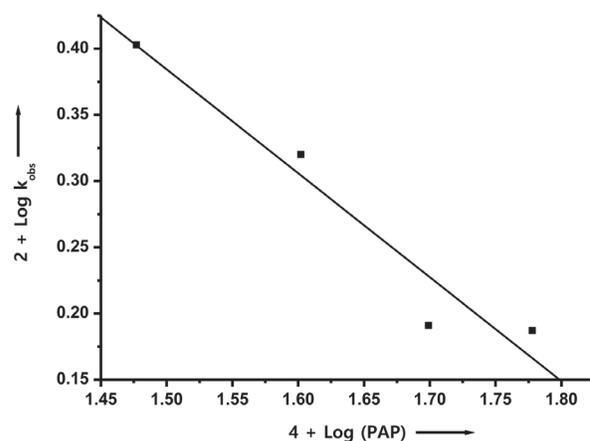


Fig. 3. Plot of $\log k_{obs}$ versus $\log [PAP]$ $[PMS] \times 10^4 = 1$ M, $pH = 7.0$, $T = 32^\circ C$, $\lambda_{max} = 395$ nm

pH Variation: The pH variation is shown in Fig. 4. It was carried out from pH 4.0 to 10.0. At low pH, the absorbance was not constant, but as the pH was made neutral, the oxidation was found to proceed in a systematic manner. It was observed that rate constant shows an abrupt rise at pH 6.0. Although at pH 6.5, the value of rate constant decreased but the rate of oxidation of PAP was found to be maximum. The rate constant was found to be maximum at pH 7.0. After this the rate of reaction decreased abruptly. The maximum value of rate constant at pH 7.0 can be attributed to the stability of mono persulfate ions $[HSO_5^-]$ (United-initiators, 2017). In pH range 6.0 to 7.0, the salt of Caro's acid, i.e. potassium mono persulfate principally exists as HSO_5^- ion and follows first order kinetics in potassium dihydrogen phosphate buffer (Donald *et al.*, 1955). At this pH, ionization must be at its peak, due to which, bulk of mono persulfate ions were produced [United-initiators, 2017]. As the pH of reaction mixture was

increased from 7.0, the stability of HSO_5^- ions decreased and hence rate was decreased. It may be due to non first order decomposition of PMS. Moreover, phosphate buffer was more favourable in acidic condition rather than basic. Hence, it can be concluded that the oxidation process of para aminophenol by using PMS was favoured either in slightly acidic condition or in neutral condition but not in basic (Donald *et al.*, 1955).

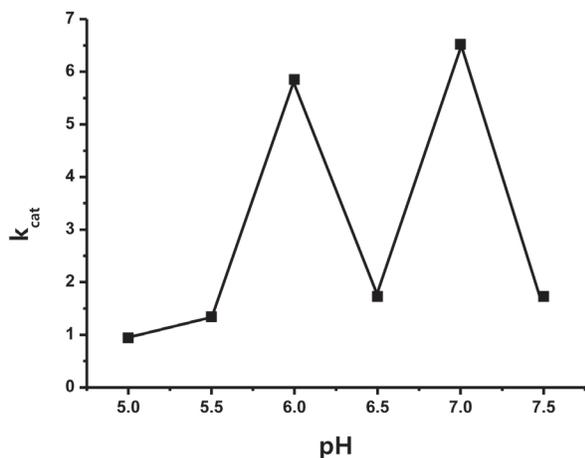


Fig. 4. Effect of the solution pH on degradation of PAP by uncatalyzed oxidation by PMS. Conditions: $[\text{PAP}] \times 10^4 = 1\text{M}$, $[\text{PMS}] \times 10^3 = 2\text{M}$, $T = 32^\circ\text{C}$, $\lambda_{\text{max}} = 395\text{nm}$

Temperature Variation: Experiments were performed in a series to assess the optimum temperature for the degradation. For this, the temperature of reaction mixture varied from 25 to 40 °C. It was observed that although oxone had some decomposition rate below 32 °C, but the activation energy required for the reaction was not enough to proceed the degradation in a systematic manner. As the temperature reaches 32 °C, oxone decomposed with a maximum rate. The rate constants observed for this process are illustrated in Table 1. Since phosphate buffering medium enhance the degradation at low temperature (Donald *et al.*, 1955), hence the variation was allowed at low temperature, below 40 °C.

Table 1.

| [PAP] (M) | Temperature (°C) | $k_{\text{obs}} (\text{sec}^{-1}) \times 10^3$ | R^2 |
|-----------|------------------|--|-------|
| 0.0001 | 32 | 1.151 | 0.980 |
| | 34 | 1.727 | 0.999 |
| | 36 | 3.378 | 0.990 |
| | 38 | 4.184 | 0.990 |

The results demonstrate that as the temperature increases the rate of degradation of PAP also increases. The apparent activation energy was calculated to be 159.92 kJ/mol. This was comparable to other compounds that were degraded by using oxone. For example, activation energies for glycine and alanine were 112.13 kJ/mol and 101.67 kJ/mol (Easwaramurthy *et al.*, 2007). An Arrhenius plot is shown in Fig. 5.

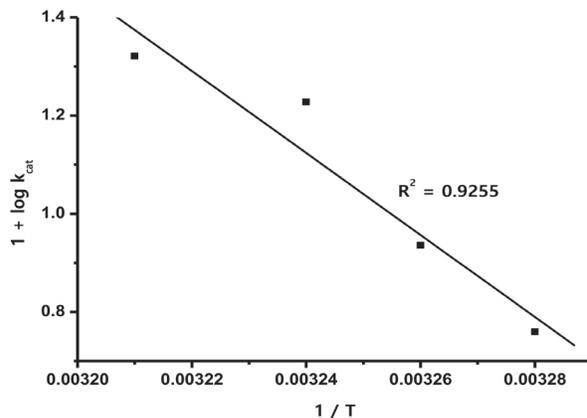


Fig. 5. Plot of $\text{Log } k_{\text{cat}}$ versus $1/T$ for PAP degradation by uncatalyzed peroxy monosulphate oxidation process. Conditions: $[\text{PAP}] \times 10^4 = 1\text{M}$, $[\text{PMS}] \times 10^3 = 2\text{M}$, $\text{pH} = 7.0$, $\lambda_{\text{max}} = 395\text{nm}$

Effect of Ionic Strength

The effect of ions on the degradation process was measured by varying the concentration of phosphate ions from 0.1M to 0.4M. It was observed that the rate of degradation is affected slightly. It may be due to the dipolar nature or zwitter ionic nature of PAP, which reacts with HSO_5^- (an ionic species) (Amis, 1966) in the reaction mixture buffered by phosphate. Moreover, it can be concluded that change in concentration of phosphate ions, does not affect the rate in very much extent, as high ionic strength is necessary for present study (Donald *et al.*, 1955). The graph is shown in Fig. 6.

Effect of Dielectric Constant: PAP exists as a neutral molecule in a solution, since it is a zwitter ion. Here, the graph had a negative slope, which depicts the reaction between an anion, i.e. HSO_5^- from PMS and PAP. Secondly, the dielectric constant of the medium had a positive effect on degradation of PAP. This may be due to the larger radius of the species formed in the transition state than the radius of HSO_5^- ion. The factor responsible for this intermediate state formation is electrostatic force of

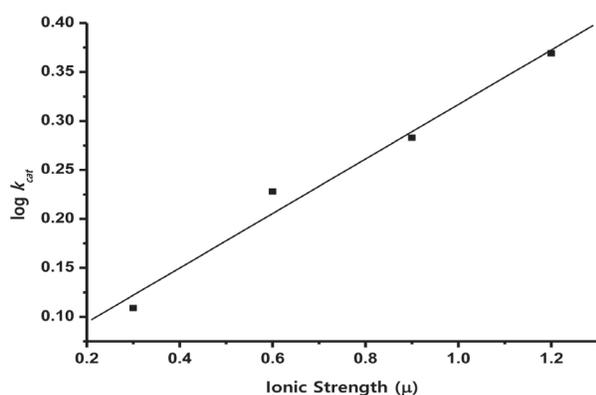


Fig. 6. Effect of Ionic strength on reaction rate [PAP] $\times 10^4 = 1.0$ M, $[\text{KHSO}_5] \times 10^3 = 2.0$ M, pH = 7.0, $\lambda_{\text{max}} = 395\text{nm}$, T = 32°C

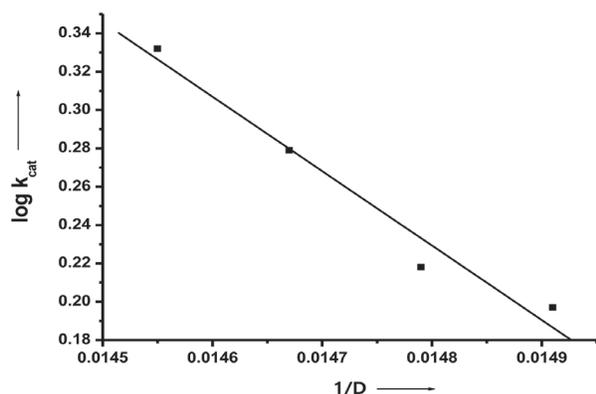


Fig. 7. Effect of Dielectric constant on reaction rate [PAP] $\times 10^4 = 1.0$ M, $[\text{KHSO}_5] \times 10^3 = 2.0$ M, pH = 6.5, $\lambda_{\text{max}} = 395$ nm, Temp.= 32 °C

attraction between them. The graph is shown in Fig. 7.

Comparative Review : Various methods have been reported which deal with removal of pollutants by generating sulfate radicals (Zhang *et al.*, 2018; Hong *et al.*, 2017; Lu *et al.*, 2019; Feng *et al.*, 2018; Lu *et al.*, 2017; Deng *et al.*, 2014). These methods can be compared with the present study in Table 2, since it

also involves the reaction between sulfate radicals and PAP during the reaction.

CONCLUSION

The aim of this research was to degrade PAP by non-toxic PMS without using any catalyst. As defined earlier, as the temperature was increased, degradation of PAP also increased. Initial concentration of PAP had a negative and PMS had a positive effect on degradation process. Hence, for 25 mL reaction mixture, the optimal conditions to degrade PAP (0.0001M) were as follows: volume of PMS was 5mL (0.01M), temperature was 32-38 °C and pH was 6.5-7.0.

REFERENCES

- Agüera, A., Pupo Nogueira, R.F. and Trovo, A.G. 2012. Paracetamol degradation intermediates and toxicity during photo-Fenton treatment using different iron species. *Water Res.* 46 : 5374-5380.
- Aguilar, C.A., Leyva, E. and Moctezuma, E. 2012. Photocatalytic degradation of paracetamol: intermediates and total reaction mechanism. *J Hazard Mater.* 243 : 130-138.
- Aissani-Benissad, F., Fourcade, F. and Yahiaoui, I. 2013. Removal of tetracycline hydrochloride from water based on direct anodic oxidation (Pb/PbO₂ electrode) coupled to activated sludge culture. *Chem Eng J.* 221 : 418-425.
- Aissani-Benissad, F., Ledjeri, A. and Yahiaoui, I. 2016. The electro/Fe³⁺/peroxydisulfate (PDS) process coupled to activated sludge culture for the degradation of tetracycline. *J Environ Manage.* 184: 249-254.
- Amis, E.S. 1966. *Solvent Effects on Reaction Rates and Mechanisms.* Academic Press, New York.
- Amrane, A., Aissani-Benissad, F., Aitali, S., Dibene, K., Khenniche, L. and Yahiaoui, I. 2019. Central composite design applied to paracetamol degradation by heat-activated peroxydisulfate oxidation process and its relevance as a pretreatment prior to a biological treatment. *Environmental Technology.* DOI: 10.1080/

Table 2.

| Authors | Target compound | Activation energy |
|----------------------------|---|--------------------|
| Rayappan S M <i>et al.</i> | Glycine (Easwaramurthy <i>et al.</i> , 2007). | 112.13 kJ/mol |
| Rayappan S M <i>et al.</i> | Alanine (Easwaramurthy <i>et al.</i> , 2007). | 101.67 kJ/mol |
| Ji <i>et al.</i> | Atrazine (Dong <i>et al.</i> , 2015) | 97.98 kJ/mol |
| Tan <i>et al.</i> | Diuron (Deng <i>et al.</i> , 2012) | 166.7 + 0.8 kJ/mol |
| Ghauch <i>et al.</i> | Naproxen (Ghauch <i>et al.</i> , 2015) | 155 + 26.4 kJ/mol |
| Ghauch <i>et al.</i> | Bisoprolol (Ghauch and Tuqan, 2012) | 119.8 + 10.8 kJ |
| Present study | Para aminophenol | 159.92 kJ/mol |

- 09593330.2019.1649308
- Andreozzi, R., Caprio, V., Marotta, R. and Vogna, D. 2003. Paracetamol Oxidation From Aqueous Solutions by Means of Ozonation and H₂O₂/UV System. *Water Research*. 37 (5) : 993-1004.
- Arias, C., Brillas, E., Cabot, P.L., Centellas, F., Garrido, J.A., Rodriguez, R.M. and Skoumal, M. 2006. Mineralization of Paracetamol by Ozonation Catalyzed with Fe²⁺, Cu²⁺ and UVA Light. *Applied Catalysis, B: Environmental*. 66(3-4): 228-240.
- Arias, C., Brillas, E., Cabot, P.L., Centellas, F., Garrido, J.A., Rodriguez, R.M. and Sires, I. 2005. Mineralization of Paracetamol in Aqueous Medium by Anodic Oxidation with a Boron-Doped Diamond Electrode. *Chemosphere*. 58(4): 399-406.
- Boxall, A. 2008. "Report on Environmental Impact and Health Effects of PPs." *Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters*, pp. 1-28.
- Brorström Lundén, E., Kaj, L., Remberger, M., Viktor, T., Woldegiorgis, A. and Wiklund, P. 2009. Anti-Inflammatory and Analgesic Drugs in WWTP Influent and Effluent Streams and the Occurrence in the Aquatic Environment. *IVL Swedish Environmental Research Institute Report*. 38 pages.
- Calder, I.C., Funder, C.C., Green, C.R., Ham, K.N. and Tange, J.D. 1971. Comparative nephrotoxicity of aspirin and phenacetin derivatives. *Br. Med. J.* 4:518-521.
- Carter, K.E. and Matzek, L.W. 2016. Activated persulfate for organic chemical degradation: a review. *Chemosphere*. 151 : 178-188.
- Cren-Olivé, C., Grenier-Loustalot, M.F. and Vulliet, E. 2011. Occurrence of Pharmaceuticals and Hormones in Drinking Water Treated from Surface Waters. *Environmental Chemistry Letters*. 9 : 103-114.
- Crimi, M., Petri, B. and Tsitonaki, A. 2010. In situ chemical oxidation of contaminated soil and groundwater using persulfate: a review. *Crit Rev Env Sci Tech*. 40 : 55-91.
- Deng, J., Gao, N. and Shao, Y. 2014. Zero-valent iron/persulfate (Fe⁰/PS) oxidation Acetaminophen in water. *Int J Environ Sci Technol*. 11 (4) : 881-890.
- Deng, Y., Gao, N. and Tan, C. 2012. Heat-activated persulfate oxidation of diuron in water. *Chem Eng J*. 203 : 294-300.
- Donald, L., Balla N.D., John, O. Edwards, 1955, The Kinetics and Mechanism of the Decomposition of Caro's Acid. I.
- Dong, C., Ji, Y. and Kong, D. 2015. Heat-activated persulfate oxidation of atrazine: implications for remediation of groundwater contaminated by herbicides. *Chem Eng J*. 263 : 45-54.
- Duan, X., Kang, J. and Sun, H. 2015. Insights into heterogeneous catalysis of persulfate activation on dimensional-structured nanocarbons. *ACS Catal*. 5: 4629-4636.
- Easwaramurthy, D., Murugesan, V., Palanichamy, M. and Rayappan, S.M. 2007. Kinetics of Ag(I) catalyzed oxidation of amino acids by peroxomonosulphate, *Inorganic Chemistry Communications*. 13 : 131-133.
- Feng, Y., Liu, Y., Peng, S. 2018. Applicability study on the degradation of Acetaminophen via an H₂O₂/PDS-based advanced oxidation process using pyrite. *Chemosphere*. 212 : 438-446.
- Fourcade, F., Ferrag-Siagh, F. and Soutrel, I. 2013. Tetracycline degradation and mineralization by the coupling of an electro-Fenton pretreatment and a biological process. *J Chem Technol Biotechnol*. 88: 1380-1386.
- Ghauch, A. and Tuqan, A.M. 2012. Oxidation of bisoprolol in heated persulfate/H₂O systems: kinetics and products. *Chem Eng J*. 183 : 162-171.
- Ghauch, A., Kibbi, N. and Tuqan, A.M. 2015. Naproxen abatement by thermally activated persulfate in aqueous systems. *Chem Eng J*. 279 : 861-873.
- Green, C.R., Ham, K.N. and Tange, J.T. 1969. Kidney lesions induced in rats by *p* aminophenol. *Br. Med. J.* 1 : 162-164.
- Grübel, K., Lutze, H.V. and WacBawek, S. 2017. Chemistry of persulfates in water and wastewater treatment: a review. *Chem Eng J*. 330 : 44-62.
- Hatakka, H., Kornev, I., Louhi-Kultanen, M., Panorel, I. and Preis, S. 2013. Oxidation of Aqueous Paracetamol by Pulsed Corona Discharge, *Ozone: Science & Engineering: The Journal of the International Ozone Association*. 35(2) : 116-124.
- Hong, J., Zhang, Q. and Zhang, Y. 2017. Sulfate radical degradation of Acetaminophen by novel iron-copper bimetallic oxidation catalyzed by persulfate: mechanism and degradation pathways. *Appl Surf Sci*. 422 : 443-451.
- Kadji, H., Ledjeri, A., Yahiaoui, I. 2017. Combination of the Electro/Fe³⁺/peroxydisulfate (PDS) process with activated sludge culture for the degradation of sulfamethazine. *Environ Toxicol Pharmacol*. 53 : 34-39.
- Lu, J., Jiang, M. and Ji, Y. 2017. Bicarbonate-activated persulfate oxidation of Acetaminophen. *Water Res*. 116 : 324-331.
- Lu, X., Wang, S. and Wu, J. 2019. Removal of Acetaminophen in the Fe²⁺/persulfate system: kinetic model and degradation pathways. *Chem Eng J*. 358 : 1091-1100.
- Madi, K., Yahiaoui, I. and Yahia Cherif, L. 2018. The feasibility of combining an electrochemical treatment on a carbon felt electrode and a biological treatment for the degradation of tetracycline and tylosin- application of the experimental design methodology. *Sep Sci Technol*. 53 : 337-348.
- Mahvi, A.H., Nasser, S. and Safari, G.H. 2015. Optimization of sonochemical degradation of

- tetracycline in aqueous solution using sono-activated persulfate process. *J Environ Health Sci Eng.* :1-15.
- Min, S., Risheng, Y., Yahua, Y., Shengsong, D. and Wenxia, G. 2007. Degradation of 4-aminophenol by hydrogen peroxide oxidation using enzyme from *Serratia marcescens* as catalyst, *Front. Environ. Sci. Engin. China.* 1(1): 95-98.
- Quan, X., Zhao, J. and Zhang, Y. 2010. Enhanced oxidation of 4- chlorophenol using sulfate radicals generated from zerovalent iron and peroxydisulfate at ambient temperature. *Sep Purif Technol.* 71 : 302-307.
- Ray, M.B., Yang, L. and Yu, L.E. 2009. Photocatalytic Oxidation of Paracetamol: Dominant Reactants, Intermediates, and Reaction Mechanisms. *Environmental Science & Technology.* 43(2) : 460-465. 124.
- Wp-content on Caroot by UNITED -INITIATORS dated on 08/2017.
- Zhang, Q., Dong, Z. and Zhang, Y. 2018. Degradation of Acetaminophen with ferrous/copperoxide activate persulfate: synergism of iron and copper. *Water Res.* 146 : 232-243.
-