

A REVIEW ON CATALYTIC WET PEROXIDE OXIDATION FOR THE DETOXIFICATION OF ORGANIC AQUEOUS WASTE

¹Divya S. Nair, ²Angel P Alias, ³Alekha Eldhose, ⁴Alex Saji, ⁵Asif K A

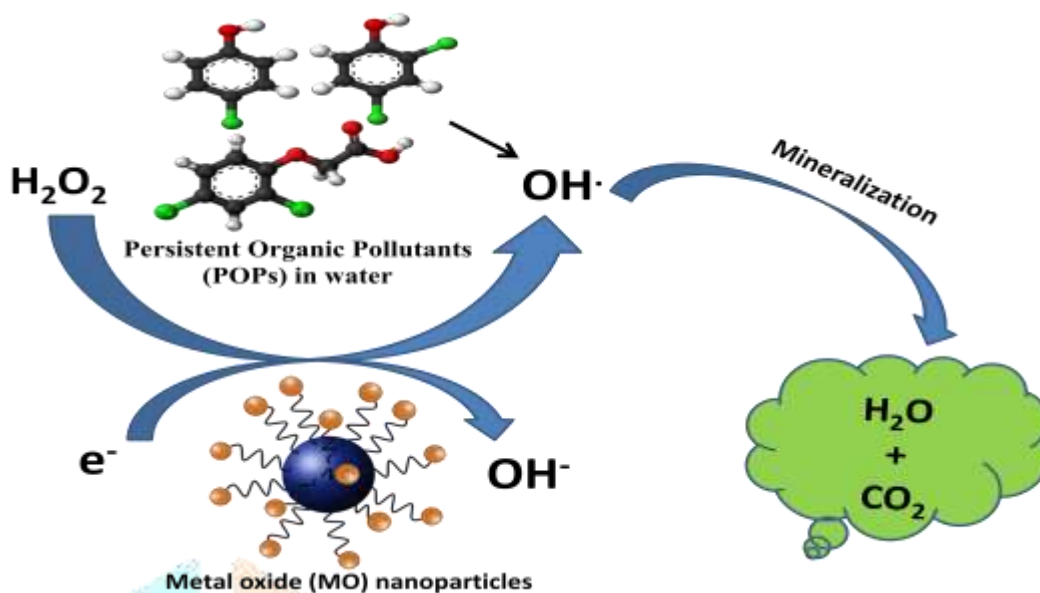
¹Assistant Professor, KCAET, KAU, Malappuram – 679573, Kerala, India.

²⁻⁵Department of Civil Engineering, Muthoot Institute of Technology and Science, Varikoli, India.

Abstract: The increase in the disposal of organic wastes into aqueous streams demands novel and economic treatment technologies for their mineralization. Advanced Oxidation Processes (AOPs) constitute a promising way for wastewater remediation and this study presents a general review on such processes with a special emphasis on Catalytic Wet Peroxide Oxidation (CWPO). Catalysis can serve as an integral green processing tool, ensuring lower operating pressure and temperature with reduction in energy requirements and facilitating waste conversion to reusable materials. CWPO stands out among other different AOPs for the effective removal of toxic and harmful pollutants from water. This review showcases impact of heterogeneously catalyzed peroxide oxidation for the removal chlorinated phenols, a group of Persistent Organic Pollutants (POPs) from water under mild conditions.

Index Terms– Advanced Oxidation Process, chlorophenols, Wet Peroxide Oxidation, Persistent Organic Pollutants

GRAPHICAL ABSTRACT



Catalytic Wet Peroxide Oxidation of chlorophenols using metal oxide nanoparticles

I. INTRODUCTION

Water is an irreplaceable basic component of life and is being polluted by different anthropogenic activities. Environmental pollution originates from various sources such as production, application and disposal of wide range of chemicals from agricultural, pharmaceutical, industrial fields etc. which badly affect the balance of hydrosphere. There are several contaminants in wastewater, with organic pollutants playing the major role. Chemical and petroleum industries generate a wide variety of highly toxic organic wastes. Many kinds of organic compounds, such as PCBs, pesticides, herbicides, phenols, polycyclic aromatic hydrocarbons (PAHs), aliphatic and heterocyclic compounds are included in this category [1-2].

Removal of toxic organic compounds from aqueous streams has become a crucial problem during the last decade. Among organic pollutants, phenol and its derivatives are considered as unavoidable raw materials in petrochemical, chemical and pharmaceutical industries [3-4]. Some of the most toxic members of phenolic compounds and its chlorinated and nitro-substituted derivatives are considered as major intermediates for the synthesis of pesticides and anti-bacterials. Among different classes of pollutants, chlorophenols (CPs) are a group of priority toxic pollutants and they have prolonged persistence in the environment and biomagnified through food chain, causing serious health problems. It also has the potential to decrease the growth and reproductive capacity of aquatic organisms. Chlorinated derivatives of aromatic compounds are the major intermediates and/or the main decomposition product of many of the synthetic pesticides. The inhibitory effects of phenol have been reported for concentrations larger than 500 ppm, and chlorinated derivatives exhibit an even larger bio-toxicity at similar concentrations [5]. These compounds can persist in the environment and bio-

magnified through the food chain and hence are considered as priority toxic pollutant because of their high toxicity and non-biodegradability and hence are listed by both the US-EPA Clean Water Act and the European Union Decision 2455/2001/EC. Chlorophenols especially chlorine at the fourth position (4-chlorophenol and 2,4-dichlorophenol) and 2,4-dichlorophenoxy acetic acid (2,4-D) have been recognized as the most important among them. 2,4-D is used as a herbicide which control the broad-leaf weeds in agriculture and is used up worldwide in an uncontrolled manner. The wide spread use of 2,4-D leads to great environmental impact because of its easy solubility in soil, leading to soil and water contamination and other related health problems. 2,4-dichlorophenol is the prime precursor for the manufacture of 2,4-D and so is the major transformation product resulted by the solar photolysis and microbial action to 2,4-D in soil or natural water. In people, developmental, behavioral, neurologic, endocrinal, reproductive and immunologic adverse health effects have also been linked to these compounds. Environmental concerns have led to extensive research on the safe and effective removal of hazardous organic compounds from aqueous streams [5].

Environmental concerns have led to extensive research on the safe and effective removal of hazardous organic compounds from aqueous streams. An ideal waste treatment process must completely mineralize toxic species without leaving behind any hazardous residues in a cost-effective manner. Numerous classes of abatement techniques including biological, thermal and physico-chemical treatments have been developed in the last few years for the detoxification of organic pollutants. Biological treatments usually require a long residence time for the micro-organisms to degrade the pollutant, because they are affected by chlorophenol toxicity. Thermal treatments present considerable emission of hazardous compounds and cause secondary pollution. Physico-chemical processes such as flocculation, precipitation etc. require post treatment procedure to remove the pollutant from the newly contaminated environment [6-8]. Advanced Oxidation Processes (AOP's) is an efficient alternative for the complete removal and detoxification of toxic organic pollutants.

II. ADVANCED OXIDATION PROCESSES

During the last few years, a series of new methods for water and wastewater purification, called Advanced Oxidation Processes (AOP), have received considerable attention. The concept of AOP was established by Glaze et al. in 1987 [9]. AOPs were defined as the oxidation processes, which generate highly reactive hydroxyl radicals in sufficient quantity to affect water treatment. Many systems like Homogeneous Fenton, photo-Fenton, sonolysis, air/ozone oxidation, photocatalysis, peroxide oxidation etc are considered under this broad definition of AOP. Many of them use a combination of strong oxidants, e.g. O_3 and H_2O_2 , catalysts, e.g. transition metal ions or photocatalyst, and irradiation, e.g. ultraviolet (UV), ultrasound (US), or electron beam (Fig.1).

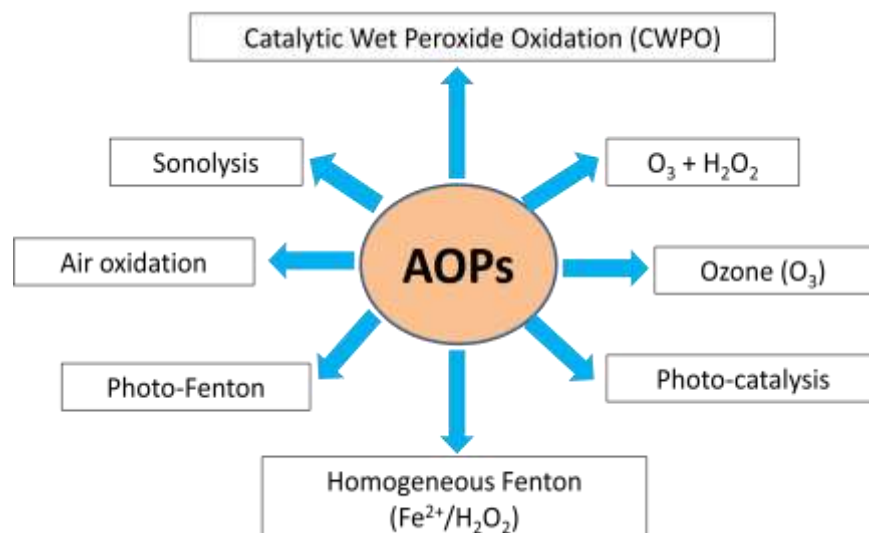


Fig 1 Advanced Oxidation Processes

The main advantage of these methods is its increased rates of pollutant oxidation, concerning water quality variations, flexibility and small dimension of the equipment. The main disadvantages associated with them are the relatively high treatment costs and special safety requirements due to the involvement of highly reactive chemicals (ozone, hydrogen peroxide) and high-energy sources (UV lamps, electron beams, radioactive sources etc). The hydroxyl radical ($\text{OH}\cdot$) is a powerful and non-selective chemical oxidant with high electrode potential, acts very rapidly with organic compounds and lead to their complete oxidation without causing secondary pollution. Wet Air Oxidation (WAO) and Wet Peroxide Oxidation (WPO) are of special interest under this category [10-11], as they enable complete detoxification of organic pollutants to benign products. WPO takes the advantage of employing hydrogen peroxide as the liquid oxidant and also by avoiding gas-liquid mass transfer limitations compared to WAO. Also the severe operating conditions of temperature ($200\text{-}300^\circ\text{C}$) and pressure ($20\text{-}80$ bar) make WAO more capital intensive than WPO [12]. Catalysis is an integral component in green processing technology, serving as an important tool to support sustainable maintenance and development. Incorporating catalysts in WAO and WPO can enhance treatment performance at even milder operating conditions, thus making processes more economic and attractive [12,13].

In the field of nanocatalysis, a wide variety of homogeneous and heterogeneous catalytic materials have been experimented. The activity and selectivity of a catalytic material can be improved by the tailored design of materials dimension with the desired structures and the desired dispersion of active sites. Considering the economical challenges of developing cheaper, readily available, stable, recyclable materials with increased productivity and selectivity for catalytic reactions is ever increasing in the field of science and technology to improve the quality of mankind. CWPO process is a very broad area under AOPs for the complete degradation

and removal of toxic organic compounds from aqueous streams at mild reaction conditions. Considering the toxicity and non-biodegradable nature, chlorophenols are selected as target pollutants and therefore the future discussion will be limited to the catalytic wet peroxide oxidation of chlorophenols. Only the heterogeneously catalyzed oxidation processes are reviewed here and the results of WPO of phenols and their chlorinated derivatives are compared.

III. CATALYTIC WET PEROXIDE OXIDATION OF CHLOROPHENOLS

The heterogeneous CWPO has many advantages over the classical Fenton like homogeneous catalysis, such as enhancement of catalytic activity, lack of secondary pollution because of leaching and widening of pH range and the possibility of reusing the catalyst in successive cycles [14-15]. A wide range of heterogeneous catalysts have been applied to wet peroxide oxidation process for the removal of toxic organic pollutants. They can be classified into three groups: (i) transition metals and their compounds, e.g. Fenton-like reagent, CuO and ZnO based, Pd/Mg and Pd/Fe bimetallic systems etc. (ii) solid acid catalysts (Lewis and Bronsted), e.g acid modified zirconia, tetravalent metal phosphates, heteropolyacids, tetrabutylammonium salts, perovskites and their various combinations: metals encapsulated in zeolites and aluminophosphate molecular sieves, metal ions incorporated into mesoporous silicates of different type etc [16-19]. Fenton's process has been regarded as the most economical alternative for a wide array of applications. Because of the remarkable success of Fenton reagent for phenol oxidation, extensive research is now focused on the exploration of different types of Fenton like or modified heterogeneous systems for environmental remediation. Fe(III) activated resin, Fe-ZSM-5 zeolites, Fe₂O₃/silicalite, iron-containing mesoporous mesophase materials, zero-valent iron have been developed and successfully applied for the total mineralization of phenolic compounds [20]. The products obtained from such decomposition are relatively the same, however in some cases may be formed over a much longer timescale and/or with considerably higher catalyst concentration in comparison with regular Fenton process. In general, all Fenton-like systems are reported to be applicable at low pH. Although, such working range of pH and increasing temperature favor iron leaching from the solid catalyst and may lead to the decrease in catalytic activity regarding phenol oxidation with H₂O₂ [21]. However, new findings of Huang and Huang (2008), who studied the use of highly ordered or crystalline iron oxides towards oxidation reaction at pH 4 and 30°C, reported the absence of iron leaching for this kind of structures [22]. Xu et. al reported that 5.5 and 5.7 ppm of Fe²⁺ ions leached respectively during first and second catalytic runs with zinc-aluminium ferrite [23]. Moreover, Fenton-like systems support the oxidation at neutral or nearly neutral pH. L. Djefal., synthesized Fe-MMM2 under weak acidic conditions, reported the resistance to iron leaching due to the coordination environment of Fe atoms in a mesoporous silicate [24]. Different transition metals, their oxides and possible

combinations with various supports produced a great variety of new catalytic systems developed for oxidation purpose with hydrogen peroxide at mild conditions. Bimetallic catalysts are also gaining more interest over the last several years. Such immobilized organo metallic systems as mono and bimetallic polymeric porphyrinic structures, resulted in a more efficient catalyst than the individual components, demonstrating a synergistic effect between the metal centres. Multilayered hetero bimetallic porphyrinic structures over Au surface showed up to 3.5 times higher efficiency than the corresponding monometallic structures [25]. TiO₂ species such as rutile was explored in photo-degradation and anatase in sono-degradation of phenolic compounds. However, only the combination of TiO₂, H₂O₂ and UV light/ultrasound irradiation system demonstrated significant degradation of phenol, while the catalyst alone was not able to provide satisfactory treatment efficiency [26-28]. There were some practical disadvantages associated with heterogeneous catalysts. Several traditional catalysts demonstrated relatively limited generation of radicals. A serious drawback of various developed catalytic systems was reported to be high catalyst concentration demand, reaching up to 10 g/L [29]. Catalytic oxidation of pollutants in an environment friendly manner with the minimum usage of chemicals is still a difficult task among environmentalists and investigations are still continuing in this field.

Catalytic efficiency of Al-Fe pillared clay was evaluated for wastewater treatment via a wet oxidation process employing hydrogen peroxide as the oxidant and a total elimination of phenol with significant TOC removal was observed. The reaction was carried out in the temperature range 25–90°C with catalyst loading 0–10 g/L, phenol concentration (100–2000 ppm), input hydrogen peroxide concentration (0.15–0.6 mol/L) [30]. Similarly, literatures reported the CWPO reaction of phenols and their mono, di and tri substituted derivatives over different catalysts like, Cu-Ni-Al hydrotalcite [31], Cu-Al hydrotalcite/clay composite [32]. In all these cases, reactions were performed above room temperature and the COD removal efficiency was less than 85%. Though varieties of heterogeneous materials have been experimented as catalysts for the abatement of chlorinated organic compounds, only few literatures are available describing the reaction intermediates and reaction mechanism. Naphthalene, flourene, acenaphthalene, chrysene etc have been reported as products in wet peroxide oxidation of 4-chlorophenol in literature [33].

L. Djeflal et al. reported in 2014 about the catalytic activity of nanoscale zero-valent iron (nZVI) towards groundwater and hazardous waste treatment. In their work they investigated the structural as well as surface chemistry of nZVI and made an attempt to understand how these attributes material's reactivity [24]. The change in the polycrystalline nature of metallic iron nuclei by a disordered layer of iron oxide was noted along with a structural change experienced by Pd-doped. The translocation of Pd from the surface to regions underneath the oxide layer and the rapid loss of the Fe(0) core due to accelerated aqueous corrosion were observed towards a concomitant variation in their catalytic performance was also noted. The removal and mechanism of degradation of toxic chemicals via CWPO under mild condition at (150 °C) was reported by

Kiyokazu et al. with significant reduction in Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC). X. Qu et al. (2013) depicted the potential role of nanotechnology in wastewater treatment and remediation. The unique properties of nanomaterials and their convergence with current treatment technologies for environmental remediation presents great opportunities not only to overcome major challenges faced by existing treatment technologies, but also to provide effective and economic pathway [34].

Catalytic processes with the application of ferrite nanoparticles are in a wide range. M. Kurian et al. revealed the heterogeneous Fenton like behavior of nickel doped zinc ferrite nano particles as catalysts in the degradation of 4-chlorophenol by Wet Peroxide Oxidation reaction. The heterogeneity of the material and their catalytic efficiency for repeated applications was noted under neutral conditions. The results showed that nickel–zinc ferrite nanoparticles are efficient catalysts towards the complete degradation of 4-chlorophenol with hydrogen peroxide as oxidant and the catalysts are reusable for five successive runs without significant loss of activity. The leaching of iron was negligible even in the fifth recyclability stage which also indicated heterogeneous nature of the catalytic reaction [35]. D. S. Nair et al. (2014) outlined the destructive removal of 2,4-dichlorophenol (DCP) and 2,4-dichlorophenoxy acetic acid (2,4-D) from water by wet peroxide oxidation method at ambient conditions using cobalt substituted zinc ferrite nano composites as catalysts prepared by sol-gel auto combustion method. The results showed that the material exhibits good catalytic activity towards the destruction of 2,4-dichlorophenol and 2,4-dichlorophenoxyacetic acid at mild conditions. Leaching and structural analyses proved the structural and chemical stability for repeated applications [36]. They also investigated the efficiency of cobalt substituted zinc ferrite nanoparticles for the oxidative removal of 4-chlorophenol. Complete degradation of the pollutant within one hour at ambient temperature was reported with good recyclability [37].

IV. CONCLUSIONS

Wastewater treatment and its reuse is a very challenging task related not only to a number of benefits in regard to water management but related to its sustainable maintenance also. Immediate research must be launched in this direction so as to safeguard human health and environment. Nanomaterials, with unique physical and chemical properties have a tremendous potential for environmental remediation. Catalytic Wet Peroxide Oxidation processes represent a powerful mean for the abatement of refractory and/or toxic pollutants in wastewaters. As we have described in this review, the use of heterogeneous materials as catalysts for the complete removal of persistent organic pollutants in water via oxidation process is though an attractive way but fields are still to be discovered. The development of a stable, active and reusable material as catalyst may contribute more yield and thereby strengthen the area of catalysis.

REFERENCES

1. L. H. Kaith, W. A. Telliard, Priority pollutants I - A perspective view; *Environ Sci Technol.* 13 (1979) 416–423.
2. R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. Von Gunten, B. Wehrli. *Science* 313 (2006) 1072-1077.
3. L.H. Keith, W.A. Telliard, *Environ. Sci. Technol.* 13 (1979) 416–424.
4. M. Van den Berg, L. Birnbaum, ATC Bosveld *Environ. Health Perspect.* 106 (1998) 775-792.
5. C. N. Pope, *J. Toxicol. Env. Heal. B.* 2 (1999) 161-181.
6. A. Sharma, *Inter. J. Res. Environ. Sci. Technol.* 3 (2013) 117-121.
7. Z.M. Nagy, K. Gruiz, M. Molnar, E. Fenyvesi, *Chem. Eng.* 57 (2013) 25–35.
8. H. Movahedian, A.M. SeidMohammadi, A. Assadi, *Iran. J. Environ. Health Sci. Eng.* 6 (2009) 153-160.
9. W. H. Glaze, J. W. Kang, D. H. Chapin, *Ozone Science & Engineering*, 9 (1987) 335-342.
10. F. Luck, *Catal. Today* 27 (1996) 195–202.
11. C. W. Jones; The Royal Society of Chemistry: Thomas Graham House, Science Park, Milton Road, 1999.
12. J. Levec, A. Pintar, *Catal. Today* 124 (2007) 172–184.
13. Y. Shaoxia, *J. Hazard. Mater.* 153 (2008) 1248.
14. M. Aliabadi, S.M. Mirarefin, M. Moghadam; *J. Adv. Res.* 2 (2004) 49-53.
15. N. Daneshvar, V. Vatanpour, R.A. Khataee; *J. color sci. technol.* 1 (2008) 83-91.
16. P. Bautista, A. F. Mohedano, J. A. Casas, J. A. Zazo, J. J. Rodriguez, *J. Chem. Technol. Biotechnol.* 83 (2008) 1323–1338.
17. J. J. Pignatello, E. Oliveros, A. Mackay, *Crit. Rev. Environ. Sci. Tech.* 36 (2006) 1–84.
18. C. T. Benatti, A. C. S. Da-Costa, C. R. G. Tavares, *J. Hazard. Mater.* 163 (2009) 1246–1253.
19. E. M. Siedlecka, P. Stepnowski, *Pol. J. Environ. Stud.* 14 (2005) 823–828.
20. L. Djeflal, S. Abderrahmane, M. Benzina, M. Fourmentin, S. Siffert, S. Fourmentin, *Environ Sci. Pollut. Res* 21 (2014) 3331–3338.
21. M. Choquette-Labbé, W. A. Shewa, J. A. Lalman, S. R. Shanmugam, *Water* 2014, 6, 1785-1806.
22. Chun-Ping Huang, Yao-Hui Huang, *Appl. Catal. A: Gen.* 346 (2008) 140–148.
23. A. H. Xu, M. Yang, H. Z. Du, C. L. Sun, *Catal. Commun.* 7 (2006) 513–517.

24. L. Djeflal, S. Abderrahmane, M. Benzina, M. Fourmentin, S. Siffert, S. Fourmentin, *Environ Sci. Pollut. Res* 21 (2014) 3331–3338.
25. R. R. Carballo, V. Campodall Orto, I. N. Rezzano, *J. Molecular Catal. A: Chem.*, 280 (2008) 156–163.
26. K. Mehrotra, G. S. Yablonsky, A. K. Ray, *Ind. Eng. Chem. Res.* 42 (2003) 2273–2281.
27. C. H. Chiou, C. Y. Wu, R. S. Juang, *Chem. Eng. J.* 139 (2008) 322–329.
28. M. Kubo, K. Matsuoka, A. Takahashi, N. Shibasaki–Kitakawa, T. Yonemoto; *Ultrasonics Sonochemistry* 12 (2005) 263–269.
29. I. Fechete, Y. Wang, C. Jacques. Vedrine, *Catalysis Today* 189 (2012) 2– 27.
30. R. M. Liou, S. H. Chen, C. H. Huang, M. Y. Hung, J. S. Chang, C. L. Lai, *Water Sci. Technol.*, 61 (2010)1489-98.
31. S. Zhou, Z. Qian, T. Sun, J. Xu, C. Xia, *Appl. Clay Sci.* 53 (2011) 627-633.
32. S. Zhou, Z. Qian, T. Sun, J. Xu, C. Xia, *J. of Colloid and Interface Sci.* 357(2011)447-452.
33. R. Klaewkla, S. Kulprathipanja, P. Rangsunvigit, T. Rirksomboon, W. Rathbun, L. Nemeth; *Chem. Eng. J.* 129 (2007) 21–30.
34. X. Qu, P. J. Alvarez, Q. Li; *Water Res.* 47 (2013) 3931-3946.
35. M. Kurian, D.S. Nair, *J. Water Process Eng.* 8 (2015) 37-49.
36. D. S. Nair, M. Kurian; *J. Environ. Chem. Eng.*, 5 (2017) 964–974.
37. M. Kurian, D.S. Nair, *J. Water Process Eng.* 2 (2014) 63–69.

