"AOP Performance at Wastewater Treatment Plants: Recent Developments"

by:

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ABSTRACT:

Advanced Oxidation Processes (AOPs) are chemical treatment techniques used to remove contaminants from water and wastewater using hydroxyl radical reactions. AOPs are efficient methods for removing organic contamination not degradable by means of biological processes. AOPs are a set of treatment processes involving the production of very reactive oxygen species (hydroxyl radicals (•OH) able to destroy a wide range of organic compounds). This paper examines selected recent studies involving AOP's application for wastewater treatment. Discussions of selected reviews and summaries of results from recent reports in the technical literature are provided below. Brief descriptions of the most popular AOPs are also provided. In addition, nano zero-valent iron systems (nZVI) for degrading organic contaminants are briefly examined. Performance data is provided where available or relevant. Of particular interest are treatments for emerging contaminants. Multiple studies involving remediation of wastewater contaminated by emerging contaminants by AOP's and nZVI systems are reviewed.

Introduction

The two main techniques of reducing toxins in wastewaters are chemical neutralization and photodegradation. Advanced Oxidation Processes (AOPs) utilize one or both of these approaches in tandem. AOPs were first defined in 1987 as 'near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effect water purification' [Glaze *et al*., 1987; Munter *et al*., 2001]. AOP's are generally expensive and often applied as pre-treatment in conjunction with more conventional methods [Cesaro *et al*., 2013]. AOP treatments are divided into two categories:

1) Non-Photochemical Methods:

Ozone, Catalytic Ozone, Peroxone, Fenton systems, Ferrate

2) Photochemical Methods

Ultraviolet radiation (UV), Ozone-UV Radiation, Ozone – Hydrogen Peroxide – UV Radiation, Photocatalytic ozonation, Photo Fenton/Fenton-like Systems, Photocatalytic Oxidation (UV/TiO_2), Electron Beam Irradiation, Ultrasound/sonication

Recent research and application for municipal wastewater will be briefly discussed for each of these methods.

Emerging contaminants

Emerging contaminants are a broad group of chemicals that are extremely difficult to treat and are often unregulated, even when toxicity is well documented. Emerging contaminants endanger aquatic life and they are extremely resistant to biological degradation due to their stability [Roth *et al*., 2018]. Emerging contaminants are primarily synthetic organic chemicals that have been recently detected in natural environments [Ahmed *et al*., 2017]. Emerging contaminants are often derivatives of manufactured products which adversely affect aquatic environments, surface waters, drinking water, and soils. Endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) are two groups of emerging contaminants that have garnered significant interest in the past decade [Fast *et al*., 2017]. AOP's, and nZVI, have frequently been used to treat water tainted with emerging contaminants and recent studies involving the treatment of emerging contaminants are discussed throughout this paper.

AOP's

Ozone

Ozone (O_3) is an unstable chemical that decomposes spontaneously producing hydroxyl free radicals. Ozone's instability requires generation at the point of application for effectiveness [Cesaro *et al*., 2013]. Due to power requirements and cost, ozonation has been deemed less effective than other AOPs (including ozonation used in tandem with other processes) in the reduction of wastewater micropollutants [Prieto-Rodriguez *et al*., 2013]. Ozone has shown as much as an 8% increase in pharmaceuticals destruction when used a pre-treatment with other methods such as UV and Hydrogen Peroxide. The ozone pre-treatment also reduced energy consumption by 32% while increasing pharmaceutical deactivation [Nilsson, 2015]. One study showed significant reduction in chemical oxygen demand (COD), specific ultraviolet absorbance at 254 nm, total suspended solids (TSS), and biological oxygen demand (BOD_5). However most recent studies concentrate on ozone used in tandem with other disinfection approaches or ozone with a catalyst [Bettaller *et al*., 2005].

Catalytic Ozonation

Catalysts introduced into the ozonation process have shown greater efficiency in the degradation of many contaminants compared with ozone alone. Transition metals are commonly used for catalytic ozonation [Wang and Xu, 2012]. In one study, a synthesized nanocomposite was used for catalytic ozonation of phenol in a batch reactor. The results showed that this catalyst significantly improved the degradation of phenol compared to that of ozonation without the catalyst [Heidarizad and Sengor, 2017]. Photocatalysts are light reactive chemicals which convert photons into chemical energy. These photocatalytic ozonation process has shown success in breaking down several dozen organic contaminants [Xiao *et al*., 2017]. One particular concern is the durability of photocatalysts in wastewater application. A commonly used photocatalyst, titanium dioxide (TiO_2) was studied for its durability in a 2017 study. The study findings showed that the photocatalysts could be reused at least three times without significant loss in their activity [Mecha *et al*., 2017]. A titanium dioxide – tungsten trioxide photocatalyst was recently studied in the degradation of emerging contaminants. Significant removal of caffeine, metoprolol, and ibuprofen (up to 88%) were achieved using photocatalytic ozonation with the titanium dioxide – tungsten trioxide catalyst when compared to more conventional catalysts [Rey *et al*., 2014].

Peroxone (*Ozone / Hydrogen Peroxide*) *– E. Peroxone*

Peroxone systems produce hydroxyl radicals from the decomposition of ozone enhanced by hydrogen peroxide [Deng and Zhao, 2015]. Peroxone, as a combination of ozone and hydrogen peroxide, is a new and advanced oxidation process that can be used for the treatment of polluted soils, groundwater and wastewater. Peroxone processes have been widely used for the elimination of biological refractory compounds in municipal wastewater effluents [Liu *et al*., 2015]. In a 2017 study a number of micropollutants and bromates were targeted for destruction by a peroxone system finding similarities between with the removal rates of ozonation. These micropollutants were categorized into three groups: non-reactive compounds (i.e. amidotrizoate), moderately reactive compounds (i.e. metoprolol, acesulfame potassium, bezafibrate, and benzotriazole), and highly reactive compounds (i.e. carbamazepine and diclofenac). However, the peroxone system showed promise in the suppression of bromates [Phattarapattamawong *et al*., 2018]. A hybrid electro-peroxone (E-peroxone) system, developed in 2013, showed success in degrading carbamazepine (CBZ), an emerging contaminant derived from pain and epileptic medication [Yang *et al*., 2018; Wang *et al*., 2018]. E-peroxone systems have shown more success in the breakdown of emerging contaminants and the suppression of bromates as compared to ozonation and conventional peroxone systems. In a recent study, the E-peroxone process reduced the reaction time and electrical energy consumption required to remove 90% of all spiked pharmaceuticals from the secondary effluents as compared to ozonation [Yao *et al*., 2015]. Abatement of ozone-resistant emerging contaminants such as ibuprofen, clofibric acid, and chloramphenicol were enhanced using the E-peroxone process [Wang *et al*., 2018]. Results from a 2015 study show that the E-peroxone process increased total organic carbon (TOC) elimination rate (up to 5.5 %) when compared to conventional ozonation [Wang *et al*., 2015]. TOC's react with chlorine to form regulated and potentially carcinogenic disinfection byproducts, which are known carcinogens..

Fenton Systems / Photo-Fenton Process/ Fenton-like Systems

The most commonly used metal to activate hydrogen peroxide is iron, specifically Fe^{2+}. Ferrous ions are produced in tandem with hydroxyl radicals to deactivate contaminants. This process is known as the Fenton process [Deng and Zhao, 2015]. The Fenton process has been applied to highly loaded, refractory, toxic and discolored wastewaters with success. One drawback to the Fenton process is the excessive ferric sludge generated. A 2014 study found success in using recycled ferric sludge as a source of ferrous ions needed for the Fenton process, thereby reducing generated waste and making the process more economically and environmentally attractive [Bolabajev *et al*., 2014].

A photo-Fenton process is a solar activated technology which inactivates microorganisms by photoactivated iron species and the direct action of solar photons [García-Fernández, 2018]. Photo-Fenton systems have also shown promise in detoxifying wastewater with heavy metal contamination. This treatment is considered environmentally friendly and particularly effective in areas without access to sewage wastewater treatment facilities [Barwala and Rubina, 2017].

The Fenton process has glaring disadvantages such as high operating cost, limited optimum pH range, and (as alluded to earlier) large sludge production. The concentration range of the iron ion is 50–80 ppm for batch processes, which exceeds most regulatory requirements worldwide.

Fenton-like systems are alternative methods which replace Fe^{2+} with other catalyst such as Fe^{3+}, Cu^{2+}/Cu^{+}, schorl, pyrite, and nano zero-valent iron. Fenton-like processes comprise two categories: heterogeneous and homogeneous. Heterogeneous Fenton-like processes replace Fe^{2+} in the Fenton reagent with a solid catalyst. Homogeneous Fenton-like processes combine metal ion(s)/metal ion-organic ligand complexes and hydrogen peroxide (H_2O_2). [Wang *et al*., 2016]. One study examined the applicability of Fenton-like system in the destruction of pharmaceuticals, specifically steroid hormones. It was determined that the Fenton-like system (using Fe^{3+} as the catalyst) was an economical and sound tertiary treatment for the contaminants studied [Ifelebuegu and Ezenwa, 2011]. Fenton like processes have been successfully used to treat water contaminated from by-products of traditional Chinese medicine production [Su *et al*., 2016].

Ferrate

Ferrate treatment uses Fe(VI) to oxidize micropollutants and remove phosphate by formation of ferric phosphates [Lee, 2009]. Previous studies have shown effectiveness of ferrate(VI) in removing a broad range of water pollutants including sewage organic substances, phosphate, toxic inorganic toxins, algae, micro-organisms, and emerging pollutants [Li, 2017]. Ferrate treatment resulted in selective oxidation of phenol, olefin, amine and aniline moieties. In another study selected pharmaceuticals were spiked into effluent samples. Ferrate showed promise in the removal of suspended solids and COD. Ferrate, however, failed to react with triclocarban, three androgens, seven acidic pharmaceuticals, two neutral pharmaceuticals and erythromycin [Jiang, 2014]. Ferrate has also shown promise for removing formaldehyde [Talaiekhozani *et al*., 2016].

Ultraviolet Radiation

Ultraviolet irradiation (UV) is produced by mercury arc lamps or light-emitting diodes to breakdown contaminants and micro-organisms. UV has been used for several applications including destruction of contaminants and removal of color. One of the most popular uses of UV is the inactivation of micro-organisms. A comprehensive, two-year study in Canada examined UV's ability to destroy viruses in a wastewater stream. Some removal rates were as high as 50% from pre- to post-treatment [Qiu *et al.*, 2018]. UV light-emitting diodes (UV-LED) have shown success in micro-organism inactivation [Song *et al*., 2018]. UV is more commonly used in tandem with other processes or catalysts.

Ozone – UV (O_3/UV); *Ozone – Hydrogen Peroxide – UV* (O_3/H_2O_2/UV)

Ozone is expensive to generate and is often used in concert with ultraviolet radiation (UV). UV photons activate ozone molecules generating hydroxyl free radicals [Cesaro *et al*., 2013]. Hydrogen Peroxide (H_2O_2) is often used in tandem with UV and ozone to enhance hydroxyl free radical production. A combination O_3/UV system was compared with an ozone and a UV system in removing organic load, measured as chemical oxygen demand (COD). The removal efficiency of the combined process was higher than the sum of the removal efficiencies of ozone and UV light treatments separately [Bustos-Terrones *et al*., 2016]. Another 2016 study also found improved efficiency in the oxidation of different parabens (such as methylparaben, ethylparaben, propylparaben, and butylparaben) with the pairing of UV and ozone systems compared to an ozone system without UV [Cuerda-Correa *et al*., 2016].

A study early in 2018 examined an O_3/H_2O_2/UV system for treating contaminants in gray water. This O_3/H_2O_2/UV system was particularly effective in reducing COD [Hassanshahi and Karimi-Jashni, 2016]. Another recent study looked at bisphenol degradation with a O_3/H_2O_2/UV system. It was discovered that the addition of UV to an ozone or ozone/peroxide had little effect in the breakdown of bisphenols [Mehrabani-Zeinabad *et al*., 2016].

Photocatalytic Oxidation (UV/TiO_2)

Dating to the early 1970's, photocatalytic oxidation (UV/TiO_2) involves irradiation with near-UV light of a semiconducting catalyst (generally TiO_2) which is easily photo-excited to form electron-donating and electron-accepting sites. This permits induction of oxidation–reduction reactions. When the absorbed UV photons have an energy larger than the energy gap (between the valence and the conducting bands) of the semiconductor, electron-hole pairs are formed. These pairs either recombine or migrate to the semiconductor surface and then react with chemical species adsorbed on the surface. UV/TiO_2 has been widely applied to persistent organic pollutants (POPs). Also, this process is effective on pathogenic biologic pollutants, including viruses, bacteria, and mold [Oturan and Aaron, 2014]. In a recent study, destruction of chlorophenol was significantly improved with UV/TiO_2 as compared to TiO_2 without irradiation. TOC removal improved by 30% [Tian *et al.,* 2018].

Electron Beam Irradiation

Free radicals can be generated by the excitation of molecules using high-energy electrons. These high energy electrons can be produced by gamma ray sources or, more commonly, through electron beam accelerators. Electron beam irradiation has been applied on the industrial scale for decades. Only recently have application for municipal wastewater been explored [Oturan and Aaron, 2014]. In an accelerator, a current produces a stream of electrons which are accelerated using an electric field generated by an applied voltage [Munter *et al*., 2001]. A study using EB showed a 90% reduction in the number of coliforms during irradiation. However, COD and BOD reduction reached about 50% in another study [Emami-Meibodi *et al*., 2016].

Ultrasound/Sonication

Sonochemistry is a promising oxidation process for wastewater treatment. Cavitation forms micro-bubbles that grow to a critical size then implode. Temperatures at the collapsing bubble interface reach about 5,000^o K and pressures near 500 atmospheres with the bulk solution remaining near ambient conditions. In these highly reactive conditions, hydroxyl radicals and hydrogen ions, which are very effective in degrading organic compounds, are generated. If organic compounds are present in the treated water, these compounds are rapidly destroyed either directly or by reactions with free radicals. The intensity of cavity implosion can be controlled by process parameters such as ultrasonic frequency, ultrasonic intensity per unit volume of liquid medium, static pressure, choice of ambient gas, and addition of oxidants (e.g. H_2O_2, O_3). Ultrasound was used successfully in the removal of inorganic sulfide in a simulated wastewater [Matei and Scarpete, 2016]. Ultrasound has had mixed results when applied to various emerging contaminants. In a study from 2014 sonolytic degradation efficiencies of diclofenac and ibuprofen were 80% and 10%, respectively. The sonolytic degradation efficiency of ciprofloxacin was less than 10%. As with many AOP's, ultrasound showed greater success when coupled with other treatment methods [Yap *et al*., 2018].

Nano Zero-Valent Iron (nZVI) *Systems*

Nanoscale zero-valent iron (nZVI) particles are typically 5 – 40 nm sized FeO/Fe-oxide particles that rapidly transform contaminants to non-toxic by-products. These particles are able to effectively eliminate or neutralize certain recalcitrant pollutants in water. A study was performed in 2014 to determine the effectiveness of nZVI in removing steroidal estrogen, an emerging contaminant. Reductions in overall estrogen concentration was significant at all the tested concentrations (2 to 6 g/L) and that the removal of estrogens did not increase significantly with exposure time. Maximum estrogen removal was primarily achieved already within the first hour of interaction with nZVI particles [Jarosova *et al*., 2015]. Another application for nZVI is the removal of nitrate and phosphate from wastewater. A study described in 2017 showed that the effectiveness in removal of nitrate and phosphate by nZVI can be increased by 12% to 38% with the addition of activated carbon [Khalil *et al*., 2017].

Summary

There are virtually unlimited applications for AOPs and nZVI for wastewater treatment. AOPs and nZVI methods also show great promise in the treatment of wastewater contaminated with emerging contaminants. Ultrasound performed well in the deactivation of pharmaceuticals according to recent research. In recent years ozone has shown effectiveness in deactivating pharmaceuticals and reducing COD, BOD, and suspended solids, while reducing energy costs. Ferrate has also showed promise in the reduction of COD as has UV. UV, particularly UV with ozone or peroxide, showed effectiveness in treating pollutants in graywater and the breakdown of bisphenols. In a 2013 study, catalytic ozone showed contaminant removal of up to 88% compared to conventional methods. Research within the last half decade showed that peroxone and E. peroxone improved ozone effectiveness in contaminant destruction while reducing cost compared to ozone alone. Recent studies involving Fenton processes have shown promise in the treatment of metal ions and pharmaceuticals. Contemporary studies have shown success in the deactivation of biological pathogens by UV/TiO_2. Electron beam irradiation showed effectiveness in the reduction of coliforms. Nanoscale zero-valent iron systems were effective in estrogen removal according to the findings of a five-year old study. When multiple methods are applied in tandem removal efficiencies improve significantly. Also, when multiple methods are used simultaneously, power demands decrease for the same level of contaminant destruction. What this implies is that there is a virtually unlimited number of process combinations which are more efficient in reducing contaminants and use less energy. To suggest that there is plenty of opportunity for research in AOP's and nZVI in the destruction of wastewater contaminants, particularly emerging contaminants, is a phenomenal understatement.

References

Ahmed, M. B., J. L. Zhou, H. H. Ngo, W. Guo, N. S. Thomaidis, and Jiang Xu, 2017. "Progress in the Biological and Chemical Treatment Technologies for Emerging Contaminant Removal from Wastewater: A Critical Review", ***Journal of Hazardous Materials***, ***323***: 274–298.

Barwala, A., and R. Chaudhary, 2017. "Effectiveness of Solar Photo-Fenton Process for Simultaneous Detoxification of Heavy Metals and Disinfection in Municipal Wastewater by Using Response Surface Method", ***Environmental Progress and Sustainable Energy***, ***36*** (2): 448–459.

Bataller, M., E. Veliz, L. A. Fernandez, C. Hernandez, I. Fernandez, C. Alverez, and E. Sanchez, 2005. “Secondary Effluent Treatment of Ozone”, ***IOA* 17th *World Ozone Congress***, Strasbourgh, France, (August 22–25).

Bolobajev J., E. Kattel, M. Viisimaa, A. Goi, M. Trapido, T. Tenno, and N. Dulova, 2014. “Reuse of Ferric sludge as an Iron Source for the Fenton-based Process in Wastewater Treatment”, ***Chemical Engineering Journal***, ***255***: 8–13.

Bustos-Terrones, B., J.G. Rangel-Peraza, A. Sanhouse, E.R. Bandala, and L.G. Torres, 2016. “Degradation of Organic Matter from Wastewater Using Advanced Primary Treatment by O_3 and O_3/UV in a Pilot Plant”, ***Physics and Chemistry of the Earth***, ***91***: 61–67.

Cesaro, A., V. Naddeo, and V. Belgiorno, 2013. “Wastewater Treatment by Combination of Advanced Oxidation Processes and Conventional Biological Systems,” ***J. Biorem. Biodeg.***, ***4***: 8–15.

Cuerda-Correa, E. M., J. R .Domínguez, M. J. Muñoz-Peña, and T. Gonzaĺez, 2016. “Degradation of Parabens in Different Aqueous Matrices by Several O_3-Derived Advanced Oxidation Processes”, ***Ind. Eng. Chem. Res.***, ***55***: 5161−5172.

Deng, Y., and R. Zhao, 2015. “Advanced Oxidation Processes (AOPs) in Wastewater Treatment”, ***Curr. Pollution Rep.***, ***1***: 167–176.

Emami-Meibodi, M., M. R. Parsaeian, R. Amraei, M. Banaei, F. Anvari, S.M.R. Tahami, B. Vakhshoor, A. Mehdizadeh, N. Fallah Nejad, S.P. Shirmardi, S.J. Mostafavi, and S.M.J. Mousavi, 2016. “An Experimental Investigation of Wastewater Treatment Using Electron Beam Irradiation”, ***Radiation Physics and Chemistry***, ***125***: 82–87.

Fast, S.A., V. G. Gude, D. D. Truax, J. Martin, and B. S. Magbanua, 2017. “A Critical Evaluation of Advanced Oxidation Processes for Emerging Contaminants Removal”, ***Environ. Process.***, ***4***: 283–302.

García-Fernández, I., 2018. “Inactivation of E. coli and E. faecalis by Solar Photo-Fenton with EDDS Complex at Neutral pH in Municipal Wastewater Effluents”, ***Journal of Hazardous Materials***, https://doi.org/10.1016/j.jhazmat.2018.07.037.

Glaze, W.H., J.W. Kang, and D.H. Chapin, 1987. “The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation”, ***Ozone*: *Science & Engineering***, ***9***: 335–352.

Hassanshahi, N., and A. Karimi-Jashni, 2018. “Comparison of Photo-Fenton, O_3/H_2O_2/UV and Photocatalytic Processes for the Treatment of Gray Water”, ***Ecotoxicology and Environmental Safety***, ***161***: 683–690.

Heidarizad, M., and S.S. Sengor, 2017. “Graphene Oxide/Magnesium Oxide Nanocomposite: A Novel Catalyst for Ozonation of Phenol from Wastewater”, ***World Environmental and Water Resources Congress***, Sacramento, CA, (May 21–25).

Ifelebuegu, A.O., and C.P. Ezenwa, 2011. “Removal of Endocrine Disrupting Chemicals in Wastewater Treatment by Fenton-Like Oxidation”, ***Water Air Soil Pollut.***, ***217***: 213–220.

Jarosova, B., J. Filip, K. Hilscherova, J. Tucek, Z. Simek, J. P. Giesy, R. Zboril, and L. Blaha, 2015. "Can Zero-Valent Iron Nanoparticles Remove Waterborne Estrogens?", ***Journal of Environmental Management***, ***150***: 387-392.

Jiang, J., 2014. "Advances in the Development and Application of Ferrate (VI) for Water and Wastewater Treatment", ***J. Chem. Technol. Biotechnol.***, ***89***: 165–177.

Khalil, A.M.E., O. Eljamal, T.W.M. Amen, Y. Sugihara, and N. Matsunaga, 2017. "Optimized Nano-Scale Zero-valent Iron Supported on Treated Activated Carbon for Enhanced Nitrate and Phosphate Removal from Water", ***Chemical Engineering Journal***, ***309***: 349–365

Lee,Y., S.G. Zimmermann, A.T. Kieu, and U.V. Gunten, 2009. "Ferrate (Fe (VI)) Application for Municipal Wastewater Treatment: A Novel Process for Simultaneous Micropollutant Oxidation and Phosphate Removal", ***Environ. Sci. Technol.***, ***43***: 3831–3838.

Li, N., 2017. "Ferrate as a New Treatment Chemical for Removal of Effluent Organic Matter (EfOM) and Emerging Micro-Pollutants in Treated Municipal Wastewater for Water Reuse", Theses, Dissertations and Culminating Projects. 37, Montclair State University, Montclair, NJ.

Liu, Y., J. Jiang, J. Ma, Y. Yang, C. Luo, X. Huangfu, and Z. Guo, 2015. "Role of the Propagation Reactions on the Hydroxyl Radical Formation in Ozonation and Peroxone (Ozone/Hydrogen Peroxide) Processes", ***Water Research***, ***68***: 750–758.

Matei, N., and D. Scarpete, 2016. "Assessment of Inorganic Sulfide Removal from Simulated Wastewater by Ultrasound", ***International Journal of Trend in Research and Development***, ***3*** (4): 2394-9333.

Mecha, A.C., M.S. Onyango, A.i Ochieng, and M.N.B. Momba, 2017. "Ultraviolet and Solar Photocatalytic Ozonation of Municipal Wastewater: Catalyst Reuse, Energy Requirements and Toxicity Assessment", ***Chemosphere***, ***186***: 669–676.

Mehrabani-Zeinabad, M., G. Achari, and C.H. Langford, 2016. "Degradation of Bisphenol S Using O_3 and/or H_2O_2 with UV in a Flow-through Reactor", ***J. Environ. Eng.***, ***142*** (8): 06016004 1–4.

Munter, R., S. Preis, J. Kallas, M. Trapido, and Y. Veressina, 2001. "Advanced Oxidation Processes (AOPs): Water Treatment Technology for the Twenty-first Century", ***Kemia-Kemi***, ***28***: 5.

Nillson, F., 2015. "Application of Ozone in Wastewater Treatment for Mitigation of Filamentous Bulking Sludge & Reduction of Pharmaceutical Discharge", Ph.D.Dissertation, Lund University. Lund, Sweden.

Oturan, M.A., and J. Aaron, 2014. "Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review", ***Critical Reviews in Environmental Science and Technology***, ***44***: 2577–2641.

Phattarapattamawong, S., A.M. Kaiser, E. Saracevic, H.P. Schaar, and J. Krampe, 2018. "Optimization of Ozonation and Peroxone Process for Simultaneous Control of Micropollutants and Bromate in Wastewater", ***Water Sci. Technol.***, ***2***: 404–411.

Prieto-Rodriguez, L., I. Oller, N. Klamerth, A. Aguera, E.M., Rodrıiuez, and S. Malato, 2013. “Application of Solar AOPs and Ozonation for Elimination of Micropollutants in Municipal Wastewater Treatment Plant Effluents”, ***Water Research***, ***47:*** 1521–1528.

Qiu, Y., Q. Li, B.E. Lee, N.J. Ruecker, N.F. Neumann, N.J. Ashbolt, and X. Pang, 2018. “Inactivation of Human Infectious Viruses at Two Full-Scale Wastewater Treatment Plants in Canada”, ***Water Research***, ***147***: 73–81, doi: https://doi.org/10.1016/j.watres.2018.09.057.

Rey, A., P. García-Munoz, M.D. Hernández-Alonso, E. Mena, S. García-Rodríguez, and F.J. Beltrán, 2014. “WO_3–TiO_2 Based Catalysts for the Simulated Solar Radiation Assisted Photocatalytic Ozonation of Emerging Contaminants in a Municipal Wastewater Treatment Plant Effluent”, ***Applied Catalysis B*: *Environmental***, ***154–155***: 274–284.

Talaiekhozani, T., M. Salari, M.R. Talaei, M. Bagheri, and Z. Eskandari, 2016. “Formaldehyde Removal from Wastewater and Air by Using UV, Ferrate(VI) and UV/ferrate(VI)”, ***Journal of Environmental Management***, ***184***: 204–209.

Tian, M., S.S. Thind, J.S. Dondapati, X. Li, and A. Chen, 2018. “Electrochemical Oxidation of 4-Chlorophenol for Wastewater Treatment Using Highly Active UV Treated TiO_2 Nanotubes”, ***Chemosphere***, ***209***: 182–190.

Song, K., F. Taghipour, and M. Mohseni, 2018. “Microorganisms Inactivation by Continuous and Pulsed Irradiation of Ultraviolet Light-emitting Diodes (UV-LEDs)”, ***Chemical Engineering Journal***, ***343***: 362–370.

Su, C., W. Li, Y. Lu, M. Chen, and Z. Huang, 2016. “Effect of Heterogeneous Fenton-like Pre-treatment on Anaerobic Granular Sludge Performance and Microbial Community for the Treatment of Traditional Chinese Medicine Wastewater”, ***Journal of Hazardous Materials***, ***314***: 51–58.

United States Environmental Protection Agency (USEPA), 2009. “Assessing the Use and Application of Zero-Valent Iron Nanoparticle Technology for Remediation at Contaminated Sites”, Office of Solid Waste and Emergency Response Office of Superfund Remediation and Technology Innovation, U.S. Environmental Protection Agency, Washington, D.C.

Wang, H., S. Yuan, J. Zhan, Y. Wang, G. Yu, S. Deng, J. Huang, and B. Wang, 2015. “Mechanisms of Enhanced Total Organic Carbon Elimination from Oxalic Acid Solutions by Electro-Peroxone Process”, ***Water Research***, ***80***: 20–29.

Wang, J.L., and L.J. Xu, 2012. “Advanced Oxidation Processes for Wastewater Treatment: Formation of Hydroxyl Radical and Application”, ***Critical Reviews in Environmental Science and Technology***, ***42*** (3): 251–325.

Wanga, N., T. Zhengb, G. Zhangb, and P. Wang, 2016. “A Review on Fenton-like Processes for Organic Wastewater Treatment”, ***Journal of Environmental Chemical Engineering***, ***4***: 762–787.

Wang, Y., G. Yu, S. Deng, J. Huang, and B. Wang, 2018. “The Electro-Peroxone Process for the Abatement of Emerging Contaminants: Mechanisms, Recent Advances, and Prospects”, ***Chemosphere***, ***208***: 640–654.

Xiao, J., Y. Xie, and H. Cao, 2015. "Organic Pollutants Removal in Wastewater by Heterogeneous Photocatalytic Ozonation", ***Chemosphere***, ***121***: 1–17.

Yanga B., J. Deng, G. Yu, S. Deng, J. Lia, C. Zhu, Q. Zhuo, H. Duan, and T. Guo, 2018. "Effective Degradation of Carbamazepine Using a Novel Electro-Peroxone Process Involving Simultaneous Electrochemical Generation of Ozone and Hydrogen Peroxide", ***Electrochemistry Communications***, ***86***: 26–29.

Yao, W., X. Wang, H. Yang, G. Yu, S. Deng, J. Huang, B. Wang, and Y. Wang, 2016. "Removal of Pharmaceuticals from Secondary Effluents by an Electro-Peroxone Process", ***Water Research***, ***88***: 826–835.

Yap, H.C., Y.L. Pang., S. Lim, A.Z. Abdullah, H.C. Ong, and C.H. Wu, 2018. "A Comprehensive Review on State-of-the-Art Photo-, Sono-, and Sonophotocatalytic Treatments to Degrade Emerging Contaminants", ***Int. J. Environ. Sci. Technol.***,1–28, https://doi.org/10.1007/s13762-018-1961-y.

Table 1. AOP Application/performance in treating municipal wastewaters.

Study Reference	Treatment technique	Pilot/lab/full scale study	Contaminants	Results/Findings
Nillson 2015	Ozone	Pilot	Pharmaceuticals	8% increase in contaminant reduction with 32% energy reduction
Heidarizad and Sengor, 2017	Catalytic Ozonation	Laboratory	Phenols	Reduction of Phenols improved over ozonation
Mecha *et al.*, 2017	Catalytic Ozonation	Laboratory/full	Phenols	photocatalysts can be reused at least three times without significant loss of activity
Rey *et al.*, 2014	Catalytic Ozonation	Laboratory	caffeine, metoprolol, and ibuprofen	88% reduction of contaminants achieved
Liu *et al.*, 2015	Peroxone	Full	Biological refractory compounds	Showed improvement over ozone alone
Yang *et al.*, 2018	E-peroxone	Full	CBZ	99.8% removal of CBZ achieved
Yao *et al.*, 2015	E-peroxone	Laboratory	pharmaceuticals	Energy reduction of 90% achieved compared to ozonation
Wang *et al.*, 2015	E-peroxone	Laboratory	TOC	TOC reduction 5.5% greater than ozonation
Barwala and Rubina, 2017	Photo-Fenton	Full	Heavy metals	Removals between 36-100% depending on metal
Talaiekhozani *et al.*, 2016	Ferrate	Full	Formaldehyde	Nearly 100% removal in 35 minutes
Qiu *et al.*, 2018	UV	Laboratory	Viruses	50% destruction in wastewater stream

Emami-Meibodi *et al*., 2016	Electron Beam Irradiation	Pilot	Coliforms, COD, BOD	90%reduction in coliforms – 50% reductions in COD BOD
Yap *et al*., 2018	Ultrasound	Laboratory	Diclofenac, ibuprofen, and ciprofloxacin	Diclofenac reduction 80% - ibuprofen and ciprofloxacin reduction 10%.
Jarosova *et al*., 2015	nZVI	Laboratory	Estrogen	Near 100% removal in one hour.
Khalil *et al*., 2017	nZVI	Pilot	Phosphates	12-38% phosphates reduction with activated carbon