

Perspectives on Advanced Oxidation Processes for Water and Wastewater Treatments.

Santiago Esplugas, Chemical Engineering and Analytical Chemistry Dept, Universitat de Barcelona, Martí I Franques 1-6 floor 6, Barcelona, Spain.

Abstract

Nowadays, water has emerged as an increasingly precious resource profoundly impacted by the ongoing changes in global climate patterns. On one hand, it is imperative to treat the existing water sources to ensure their safety and reliability. Conversely, once water has served its primary purpose, it must undergo further treatment before being released into the environment to prevent contamination. Advanced Oxidation Processes (AOPs) have showcased their efficacy on removing contamination across a spectrum of applications, spanning from controlled laboratory experiments and pilot plant investigations to operational demonstration facilities, solidifying their potential in the evolution of next-generation water and wastewater treatment infrastructures. These AOPs play an important role in the sustainable utilization of water resources. However, several pressing challenges currently confront AOPs, including the quest for innovative photocatalytic materials, the enhancement of process efficiency, and the development of hybrid processes that integrate multiple treatment techniques to enhance better removing of contamination.

Introduction

Earth is estimated to contain around 1,386,000,000 cubic kilometers of water, predominantly concentrated in oceans, leaving a mere 2.5% as accessible freshwater for societal consumption [1]. Meeting the global challenge of ensuring a sustainable and ample water supply of requisite quality for diverse applications is paramount. On one front, society demands high quality water for drinking purposes, while on the other, the generated wastewater necessitates treatment before reintegration into the environment. Balancing these demands poses a crucial task for addressing the world's water requirements. Figure 1 illustrates a simplified water cycle, highlighting the process where environmental freshwater undergoes treatment in drinking water facilities to fulfill the needs of agriculture, industry, and domestic use, resulting in contaminated water (wastewater) that requires treatment before reentering the environment. There is also some interchange of water between agriculture, industry, and domestic and the environment.

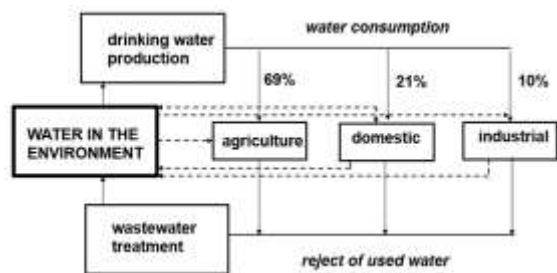


Figure 1. Simple scheme of the water cycle.

from water sources [3].

Advanced Oxidation Processes

Advanced oxidation processes (AOPs) appear first defined by Glaze in 1987 [4] "as those which involves the generation of hydroxyl radicals $^{\circ}\text{OH}$ in sufficient quantity to affect water purification. The theoretical and practical yield of $^{\circ}\text{OH}$ from O_3 at high pH, $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV and $\text{H}_2\text{O}_2/\text{UV}$ systems are.....". The hydroxyl radical possesses distinctive features, including its potent oxidizing capability (with a standard redox potential of 2.8 V), brief lifespan, remarkable chemical reactivity, non-selective reactivity as a reagent, electrophilic nature, ease of production, and ubiquitous to nature. Lately, it was known the formation of hydroperoxyl radical $^{\circ}\text{O}_2\text{H}$ less powerful than the hydroxyl. In subsequent years, various systems capable of generating hydroxyl radicals have emerged, integrating alternative oxidants such as persulfate and peroximonosulfate into Advanced Oxidation Processes. Intensive studies in heterogeneous photocatalysis started five decades ago, after the discovery of the photo-induced water splitting (yielding $^{\circ}\text{H}$ and $^{\circ}\text{OH}$ radicals) on TiO_2 electrodes [5]. First studies were focused on the utilization of solar energy for the production of hydrogen from water. One decade this research shifted towards the removal of contaminants in water, being one of the most AOPs used in Labs with few successes in reliable application in waters [6].

Among AOPs, Fenton-based techniques ($\text{Fe}^{+2}/\text{H}_2\text{O}_2/\text{UV-Vis}$) stand out as widely employed in water remediation [7][8]. Additionally, electrochemical treatments and zero valent iron contribute to hydroxyl radical generation, earning them inclusion in the category of light AOPs due to their operating conditions. There is also a group of AOPs needing hard conditions as Vacuum Ultraviolet, Ultrasounds and cavitation, electron beam, wet oxidation and non-thermal plasma with constitute the group of hot AOPs. Inside the AOPs, Zero Valent Ion, electrochemistry, sonication

and heterogeneous catalysis with TiO₂ may use the reduction capacity. Vacuum Ultraviolet, for instance, induces the photolysis of water into [•]H and [•]OH radicals, necessitating wavelengths shorter than 200 nm, which have limited penetration in pure water (in the order of micrometers), resulting in relatively low efficiencies in contaminant removal. Ultrasonic sound within a frequency range of 20 kHz - 10 MHz and hydrodynamic cavitation generate bubbles, leading to [•]OH production through the dissociation of water molecules. Electron beam irradiates electrons into the water, while non-thermal plasma produces numerous radicals in the gas phase with high oxidant power. Wet oxidation utilizes air, oxygen, or H₂O₂ to oxidize contaminants in highly polluted waters. Presently, the most widely employed AOPs fall within the category of light AOPs, including O₃-based processes, Titanium dioxide-based processes, and Fenton-based processes. Figure 2 provides a non-exhaustive list of advanced oxidation processes [9].

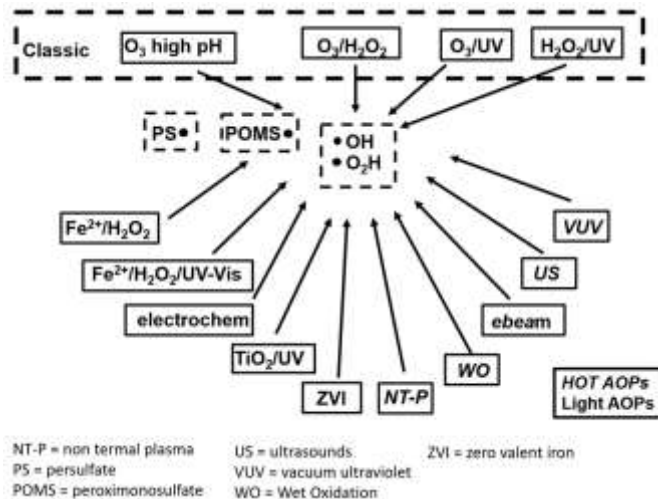


Figure 2. Not exhaustive list of AOPs [9].

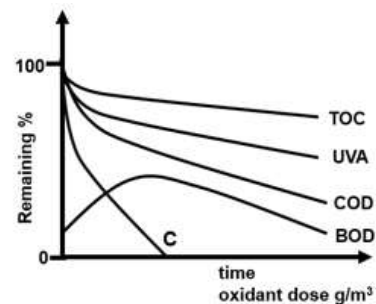


Figure 3. Oxidant dose in AOPs.

The paramount feature of AOPs lies in their ability to enhance water quality parameters upon application. Figure 3 illustrates significant water quality indicators, including contaminant concentration (C), Total Organic Carbon (TOC), Ultraviolet Absorption at 254nm (UVA), and Chemical Oxygen Demand (COD), all of which exhibit a decline with an increasing oxidant dose. In general, the Biochemical Oxygen Demand (BOD) shows an initial rise at low oxidant doses, reaching a peak value before declining at higher oxidant doses. This nuanced relationship underscores the intricate impact of oxidant dosage on water quality parameters, emphasizing the dynamic nature of AOPs in influencing and optimizing water quality outcomes. Managing toxicity is a challenging aspect of water quality, and it becomes particularly intricate in the context of AOPs. Typically, at elevated oxidant doses in AOP treatments, toxicity tends to diminish. Nevertheless, a notable caveat arises in instances where the oxidation products generated during brief AOP applications prove to be more toxic than the original substances. Future research endeavors should invest additional efforts in exploring the intricate relationship between oxidant dosage and toxicity to develop a more comprehensive understanding and effective management strategies in this critical area [10].

AOP	Advantages	Disadvantages
O ₃	Powerful oxidant (2.07 V). Has to be produced in situ. Easy to produce O ₃ from O ₂ . Selective reaction for molecular ozone and unselective for [•] OH radicals produced.	Low energy yield (5%) to produce O ₃ . Excess (residual) of O ₃ should be removed. Efficiency limited by O ₃ gas-liquid transfer and scavenging of [•] OH. Unwanted stripping of VOCs. Bromate Formation.
O ₃ /H ₂ O ₂	Additional more production of [•] OH radicals depending on O ₃ /H ₂ O ₂ ratio. High solubility of H ₂ O ₂ in water.	[•] OH scavenging by H ₂ O ₂ . Security problems in storage and manipulation of H ₂ O ₂ .
O ₃ /OH ⁻	Only production of [•] OH radicals.	Necessity to adjust pH.
O ₃ /catalyst	Additional more production of [•] OH radicals.	Necessity of removal the solid or ionic catalyst. Possible problems in reuse the catalyst.
O ₃ /UV	Synergistic effect of UV. Additional more production of [•] OH radicals.	Necessity of UV lamp equipment. Not suitable for moderate turbidity waters.

Table 1. Advantages and drawbacks of O₃ Based AOPs.

AOPs	Advantages	Disadvantages
Fenton	High performance. Operated at room temperature.	Operation at acidic pH. Security problems related to H ₂ O ₂ . Necessity of removal the FeO _x sludge.
Photo Fenton	Additional more production of °OH radicals. Use of part the visible spectrum.	Not suitable for turbidity or colored waters.

Table 2. Advantages and drawbacks of Fenton Based AOPs.

AOPs	Advantages	Disadvantages
UV/TiO ₂	No reagents needed. TiO ₂ is a low cost, non-toxic material with mechanical, thermal and chemical stability. May use part of Solar UV (4%). Good perspective in reuse TiO ₂ . No influence of pH.	Necessity of UV lamp equipment. Low quantum yield (less than 0.03) Fast recombination for hole and electron generated. Not suitable for turbidity waters. Necessity to remove the catalyst.
UV/H ₂ O ₂	H ₂ O ₂ miscible in water.	Necessity of UV lamp equipment. Very weak UV absorption except at high pH. °OH scavenging by H ₂ O ₂ . Not suitable for turbid or colored waters.
VUV	No gaseous, liquid or solid additive.	Very low wavelength (less than 200 nm). Very limited penetration depth of the photons (less than 1 mm).

Table 3. Advantages and drawbacks of UV Based AOPs.

Tables 1, 2, and 3 provide comprehensive summaries outlining the advantages and disadvantages associated with the applications of the primary ozone, Fenton, and UV-based processes in water treatment. It is important to note that the considerations for O₃, Fenton and UV extend to their respective combinations, highlighting both the synergies and limitations inherent in these combined processes. Regarding to the efficiency, the ozone-based processes look to be the most efficiency ones [11].

Innovative Advanced Oxidation Processes

Figures 4 represents earlier innovations using the solar radiation, specially UV for TiO₂ and UV-Vis for Photo Fenton [12]. The potential combination of AOPs with biological treatment also was an earlier innovation [13].

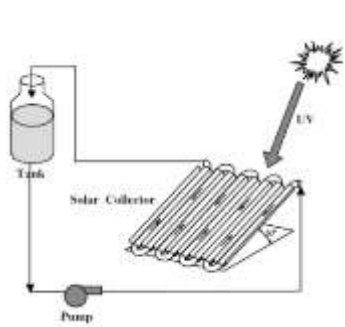


Figure 4. Solar Photoreactor.

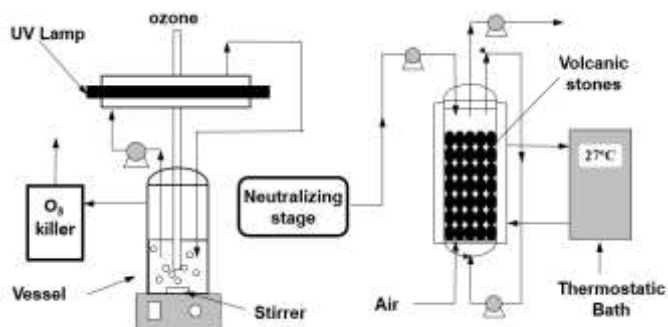


Figure 5. Ozone/UV with Biological treatment.

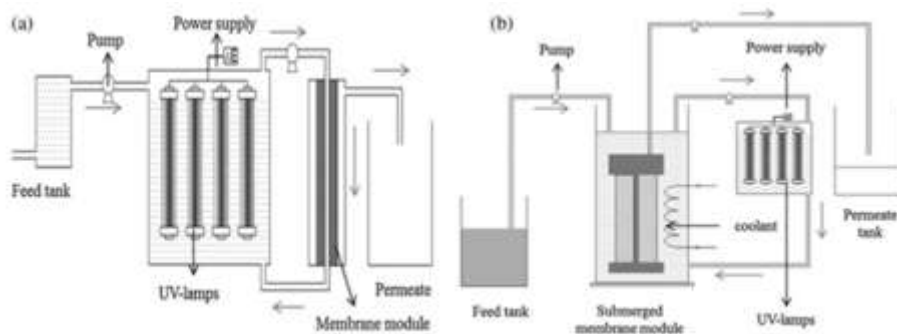


Figure 6. (a) AOP with pressurized membrane. b) AOP with submerged membrane.

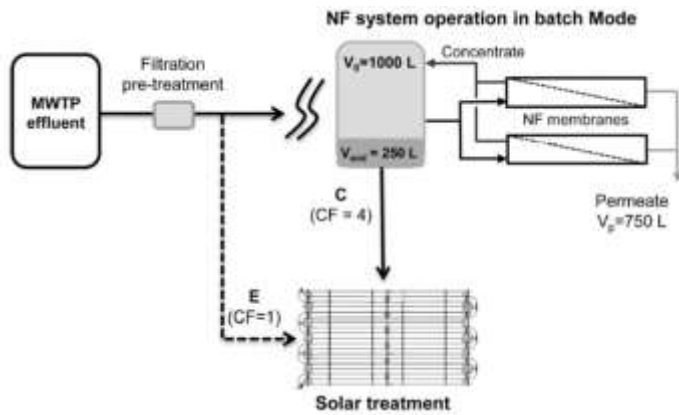


Figure 7. Solar AOP with nanofiltration.

Figure 5 showcase the hybrid system involving UV/O₃ and biological treatment [14]. Each of these schemes correspond to pilot plant experimentation conducted with wastewaters. A lot of effort has been done in the combination of AOPs with biological treatments [15]. Additional hybrid systems are presented in the figures 6 and 7. Figure 6 presents two configurations of the hybrid system involving AOPs coupled with membrane separation [16], while figure 7 depicts a solar plant coupled with a nanofiltration system operating in batch mode [17]. Conducting experiments at the laboratory or pilot plant scale with these

two distinct technologies is inherently challenging. Fortunately, contemporary times are marked by a wealth of research in this emerging and dynamic field.

Conclusions

There is still ample room for enhancing AOPs. In ozone-based methods, the production cost of O₃ remains prohibitively high (5% of the theoretical), essentially mirroring the cost of ozone itself. Furthermore, enhancing the concentration of ozone in the gas phase could significantly improve mass transfer from the gas phase to the aqueous phase. In UV-based processes, advancing LED sources could replace low-performance Hg lamps. In the case of UV/TiO₂, crucial strides must be made in designing photocatalytic materials to overcome the limitations of conventional Solar-TiO₂. For instance, a photocatalyst with minimal energy requirements for production, coupled with robust mechanical and chemical stability and a lengthy lifespan, is vital for ensuring sustainability. Additionally, the development of stable photocatalytic membranes is crucial to prevent catalyst separation from water. In Fenton-based processes, there is a pressing need to explore reliable Fenton processes at neutral pH. Finally, one should not overlook the vast potential of hybrid systems like AOPs-Bioreactor and AOPs-Separation Processes. In preparing for the future, a crucial undertaking involves evaluating the economic viability of AOPs. This necessitates a comprehensive analysis that encompasses investment costs, particularly those associated with UV sources and photoreactors, as well as operational expenses, encompassing electricity consumption, plant operations, reagents, and maintenance.

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