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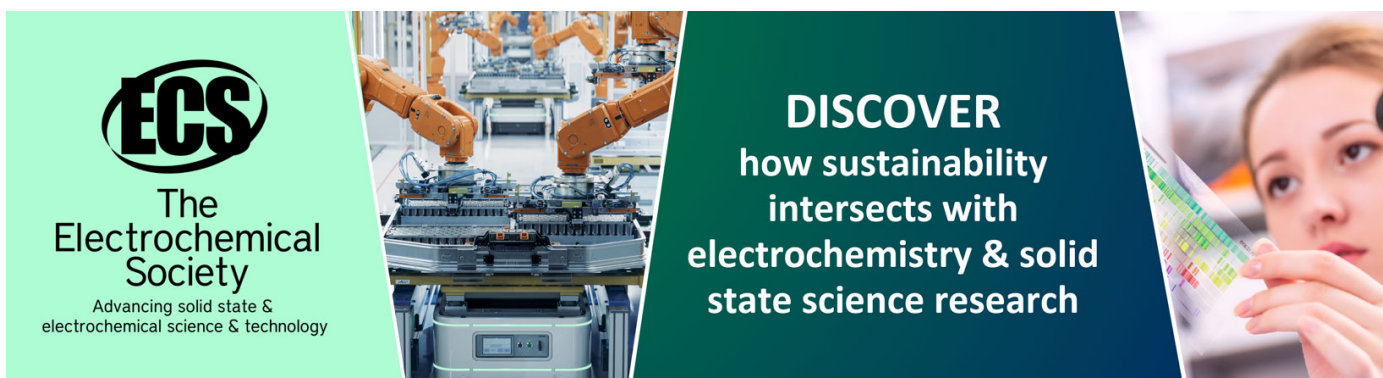
Comparison of various advanced oxidation processes used in remediation of industrial wastewater laden with recalcitrant pollutants

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Comparison of various advanced oxidation processes used in remediation of industrial wastewater laden with recalcitrant pollutants

S Krishnan^{1,2}, H Rawindran^{1,2}, C M Sinnathambi^{1,2*}, J W Lim²

¹Centre of Research Enhanced Oil Recovery (COREOR), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

²Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

*E-mail: chandro@utp.edu.my_(Chandra Mohan Sinnathambi)

Abstract. Due to the scarcity of water, it has become a necessity to improve the quality of wastewater that is discharged into the environment. Conventional wastewater treatment can be either a physical, chemical, and/or biological processes, or in some cases a combination of these operations. The main purpose of wastewater treatment is to eliminate nutrients, solids, and organic compounds from effluents. Current wastewater treatment technologies are deemed ineffective in the complete removal of pollutants, particularly organic matter. In many cases, these organic compounds are resistant to conventional treatment methods, thus creating the necessity for tertiary treatment. Advanced oxidation process (AOP), constitutes as a promising treatment technology for the management of wastewater. AOPs are characterised by a common chemical feature, where they utilize the highly reactive hydroxyl radicals for achieving complete mineralization of the organic pollutants into carbon dioxide and water. This paper delineates advanced oxidation processes currently used for the remediation of water and wastewater. It also provides the cost estimation of installing and running an AOP system. The costs are separated into three categories: capital, operational, and operating & maintenance.

1. Introduction

Wastewater is generally categorized by properties like total dissolved solids (TDS), turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved oxygen, hardness, pH, and colour. These characteristics vary between industries and also within each industry. Dissolved oxygen content in water is reduced by the presence of organic compounds. Therefore, disposing these wastewaters, without treatment, to water sources can be harmful to aquatic life.

Many types of conventional treatment methods can be used for wastewater treatment. These methods can be either physical, chemical, or biological processes, or in some cases a combination of these operations. The main purpose of wastewater treatment is to eliminate solids, organic matter and, in some cases nutrients from wastewater.

Physical treatment involves isolation or separation of the waste material from the mainstream. In this method, little or no degradation of the waste is involved, such as in coagulation, filtration, etc. On the other hand, for biological treatment, the main process involves the use of microbes to feed on the organic waste. In this case, special care like pH and aeration, should be monitored to sustain the microbes' activities.



However, there are some contaminants found in wastewater that are recalcitrant to several of the generally applied physical and/or chemical treatment processes. Chemical oxidation processes can be used to expand the current treatment processes, by transformation processes that can be used to destroy the recalcitrant compounds through oxidation and reduction reactions. The objective of this review is to investigate advanced oxidation processes that have been used for treatment of various types of contaminants, to determine the best methods for wastewater generated from different industrial processes, as well as provide a cost estimation of running an advanced oxidation system.

2. Advanced Oxidation Process

Advanced Oxidation Process (AOP) is a chemical treatment method that has been growing in the wastewater management industry. It is a highly suggested method for the removal of problematic organic matter. The basic principle of AOP involves the production of hydroxyl radicals ($\text{HO}\cdot$), which can be generated from hydrogen peroxide (H_2O_2), ozone, photo-catalysis, or oxidants in combination with using ultraviolet (UV) radiation. In some cases, two or more radical generators are used in combination. However, it is the $\text{HO}\cdot$ that is mainly responsible for the degradation of organic compounds.

The $\text{HO}\cdot$ is an unselective strong chemical oxidant. Once produced, it attacks nearly all organic complexes. Therefore, attack by the $\text{HO}\cdot$ leads to a complete breakdown of the organic compound, and as a result, AOPs diminish the concentration of the pollutant from a few hundred ppm to less than 5ppb [1]. Studies show that with AOP, organic chemicals disintegrate and become smaller and easily biodegradable. The $\text{HO}\cdot$ takes away a hydrogen atom from an organic compound (R-H) and causes the formation of an organic radical ($\cdot\text{R}$) as in Equation (1). This radical then goes through a succession of chemical reactions to form several products and by-products [2]. Theoretically, AOPs should fully mineralize organic compounds to carbon dioxide and water as illustrated in figure 1.



Advanced oxidation processes use vigorous oxidants, such as hydrogen peroxide, ozone, or Fenton's reagent to generate highly reactive intermediates. In some cases, these reagents are used in the presence of ultraviolet light, which enhances the oxidation process.

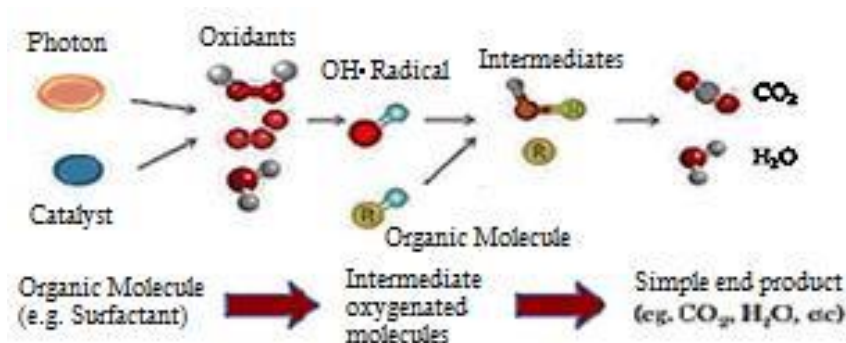


Figure 1. Principle of advanced oxidation processes [3]

The advantages of the AOPs are due to the fast reaction rates and non-selective oxidation, allowing the simultaneous treatment of multiple contaminants. Table 1 shows the relative oxidation power of the different oxidizing species, and it can be established that the oxidation power of $\text{HO}\cdot$ is relatively higher.

Table 1. Relative oxidation power [4]

Oxidizing Groups	Relative Oxidation Power
Chlorine	1.00
Hypochlorous Acid	1.10
Permanganate	1.24
Hydrogen Peroxide	1.31
Ozone	1.52
Atomic Oxygen	1.78
Hydroxyl Radical	2.05
TiO ₂ ⁺	2.35

Generally, the rate constant for the reaction of the contaminant with HO• determines the rate of destruction of a contaminant. Table 2 shows the rate constants of destruction of various compounds with ozone and hydroxyl radicals. It clearly indicates that the reaction rates are much faster with the hydroxyl radical compared to ozone.

Table 2. Reaction rate constants of ozone vs. hydroxyl radical [4]

Compound	O ₃ (M ⁻¹ s ⁻¹)	HO• (M ⁻¹ s ⁻¹)
Chlorinated alkenes	10 ³ –10 ⁴	10 ⁹ –10 ¹¹
Phenols	10 ³	10 ⁹ –10 ¹⁰
N-containing organics	10–10 ²	10 ⁸ –10 ¹⁰
Aromatics	1–10 ²	10 ⁸ –10 ¹⁰
Ketones	1	10 ⁹ –10 ¹⁰
Alcohols	10 ⁻² –1	10 ⁸ –10 ⁹

There are a few different ways by which AOPs can generate hydroxyl and other radicals [5]. Table 3 summarizes the various AOPs that have been studied for the removal of taste and odour compounds, along with the reactive species formed during each process. By studying Table 3 below, it clearly indicates that the highly reactive HO• is the main driver for all AOPs, and the effectiveness of the method depends on the efficiency by which HO• is produced. From the many AOP systems, ozonation, UV/ozone, UV/hydrogen peroxide, and photocatalysis are most frequently studied, and utilized for many applications.

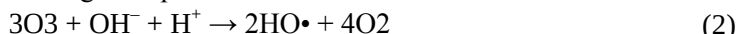
Table 3. Common AOPs and the reactive species produced in each process [5]

AOP	Reactive Species
Ozone treatment: O ₃	HO•, HO ₂ •, HO ₃ •, O ₂ ⁻ •, O ₃ ⁻ •
O ₃ /H ₂ O ₂	HO•, O ₂ ⁻ •, O ₃ ⁻ •
Fenton processes: H ₂ O ₂ /Fe ²⁺	HO•, HO ₂ •

Photo-Fenton processes	HO•
UV/O ₃ , UV/H ₂ O ₂ , UV/O ₃ /H ₂ O ₂	HO•, HO ₂ •/ O ₂ ^{-•} , O ₃ ^{-•}
V-UV (λ < 190 nm)	HO•, H ⁺ , e ⁻
Photocatalytic treatment: UV/Vis light using catalysts	HO•, h ⁺ , O ₂ ^{-•} , e ⁻ , ¹ O ₂ , HO ₂ •, HOO•
Ultrasonic treatment	HO•, •H
γ-Radiolysis	HO•, •H, e ⁻

2.1. Ozonation

The formation of radicals such as the hydroxyl radical (HO•) and superoxide radical (O₂^{-•}) occurs when ozone is added to water, through a complex series of reactions. The disintegration rate of ozone in water is better at higher pH levels [4]. A combination of reactions with molecular ozone and reactions with HO• causes the oxidation of organic species.



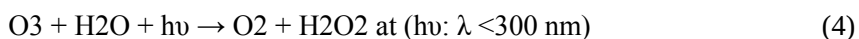
The decomposition cycle of ozone can be enhanced by the addition of hydrogen peroxide to result in the formation of HO• [6]. Hydrogen peroxide partially dissociates in water to produce the HO₂⁻. This hydroperoxide ion reacts with the ozone rapidly producing the HO•. In summary, the combination of reactions leads to the following:



Contact time, alkalinity of water, and the dose of ozone determine the performance of the process. By introducing the dose of hydrogen peroxide once the oxidation of highly reactive substances with ozone takes place, it enhances the degradation achieved. The process of ozonation by H₂O₂/O₃ systems seem to be the most established AOP in remediation for water as compared to other AOPs. Thus, there is a field-proven history of operation in the implementation of H₂O₂/O₃ systems.

The second way to speed up ozonation is by the use of homogenous or heterogeneous catalysts. Studies have been carried out with various metal oxides and metal ions, and have shown significant changes in decomposition, however only in some cases. The concentration of ozone in the inlet gas and the ozonation time has been considered as predominant factors to the enhancement of the degradation rate. Oxidation studies have been carried out on various organic contaminants using Fe₂O₃, MnO₂, TiO₂-Me, Fe²⁺, Fe³⁺, and Mn²⁺. The ozone/catalyst system appears to be more effective for the reduction of chemical oxygen demand (COD) and total organic carbon (TOC), than oxidation with ozone alone at higher pH values [7]. In experiments carried out by Horáková *et al.* [8], it was observed that decomposition of the chemicals is effectively improved by the synergistic effect of photo catalytic reactions occurring on TiO₂-photocatalyst.

Ozonation can also be enhanced when ozone decomposes by readily absorbing UV radiation (λ = 254nm), which generates H₂O₂ as an intermediate, and then decomposes to HO•. The reactions indicated in equations 4 and 5 illustrate the photolysis of ozone to generate hydrogen peroxide, which results in the production of the highly reactive HO• [9]. There are however, several oxidation mechanisms that result in the destruction of organic contaminants, but HO• is the predominant removal mechanism.



This method comprises all the organic degradation mechanisms through O₃/UV, H₂O₂/O₃ and H₂O₂/UV. It is more effective for the destruction of organic substances than using O₃ or UV alone,

and it is a more efficient way of generating HO• as compared to the UV/H₂O₂ method at equal oxidant concentrations [4].

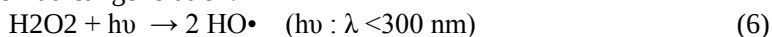
Nevertheless, this process is cost and energy intensive [9]. Furthermore, ozone methods have a potential for the formation of bromate. Interfering compounds can affect the absorption of UV radiation, thus reducing the efficiency of the system. However, this problem can be mitigated by raising the ratio of peroxide to ozone, reducing the pH, or making the concentration of other radical scavengers higher [9]. Turbidity also affects the amount of UV radiation absorbed by the ozone. The energy costs for ozone generation is the main operation expenditure for this process. The presence of bicarbonate or carbonate may act as scavengers of the HO• in natural systems is another drawback of these processes [4].

The use of AOP with ozonation has more industrial applications compared to all other AOPs in water treatment. Ozone technology has been used to manage contamination in wastewater from electroplating wastes, recycling, electronic chip manufacturing, marine aquaria, textiles, and petroleum refineries. Ozonation has also been effectively applied to the food industry, to treat wastewater from distilleries, olive mill, meat industry, and molasses [10]. There are recent applications for ozone in treating landfill leachates, rubber additive wastewaters, and detergents in municipal treatment plants [11]. An industrial scale UV/ozonation system has been set-up in Oklahoma to handle refractory organics and metal complexed cyanides [4]. Cadillac Motor Car Division in Detroit, started using ozone treatment since 1978. They have managed to maintain the total cyanide levels in the effluent below 1 mg/L [4]. Different types of ozonation systems have been studied in their ability to reduce the harmful of discharge from the pulp and paper manufacturing [12].

In the cost estimation shown by Kommineni *et al.* [9], the vendor provided estimates for their H₂O₂/O₃ system per 3.79 cubic meters of water treated. These costs varied between \$0.35 for 1380m³/h, at influent MTBE concentration of 20 µg/L and \$3.62 for 13.8m³/h, at initial Methyl tert-butyl ether (MTBE) concentration of 2,000 µg/L. In their study the capital costs for this system were higher, while the operating & maintenance (O&M) costs are suggestively lower.

2.2. AOP using hydrogen peroxide

Hydroxyl radicals are formed by the photolytic dissociation of hydrogen peroxide in water by UV irradiation at a wavelength of 254nm. This formation is indicated in Equation 6 [13]. Medium Pressure UV lamps produce a higher radical generation.



Andreozzi *et al.* [6] found that the rate of photolysis of aqueous H₂O₂ to be pH dependent, and it increases when more alkaline conditions are used. As with the UV/Ozone system, interfering compounds and turbidity can absorb the UV light, thus reducing the efficiency of the system. Hydrogen peroxide can be introduced into the system as a single dose or at many points in the system [9]. Each water source requires optimization based on lab scale testing, in order to ascertain the ideal dose of hydrogen peroxide. If there is excess H₂O₂, it reacts with other contaminants (e.g. elemental sulphur) producing complex, oxidizable materials. Vaferi *et al.* [13] concluded that this system can be used to appropriate design, and for scaling up of industrial batch reactors for wastewater treatment.

UV/H₂O₂ system is seen as a beneficial method for AOP, as it has high reaction rates, and is flexible in the design of reactors, which leads to a lesser footprint in the treatment plant. The use of ultraviolet lamps also provide disinfection of the water. Akin *et al.* [14] suggested that the polyethoxy chain of the surfactant used was more susceptible to degradation in the H₂O₂/UV treatment process. In their comparisons between H₂O₂/UV and Photo-Fenton processes, they concluded that H₂O₂/UV treatment was more efficient than the Photo-Fenton process in the overall TOC removal efficiencies of the nonylphenol polyethoxylate surfactant. This is supported in studies conducted by Antonopoulou [5], who reported that the UV/H₂O₂ process was proved effective to reduce odorous aldehyde concentrations. They further state that the findings showed that direct UV photolysis is the main mechanism involved in this degradation process.

This method for AOP treatment is cheaper because of the lower cost and easy availability of hydrogen peroxide [9]. However, this system has some drawbacks. H₂O₂ has poor UV light

absorption characteristics, thus this can be considered as wasting most of the light input. The formation of bromate for this system can hinder this process, but by lowering the pH, and increasing the peroxide to ozone ratio can reduce this problem.

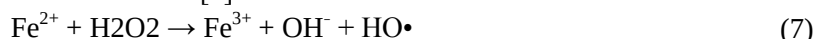
Most studies conducted on this method stress the importance of optimization of the parameters (dose and concentration of H₂O₂, concentration of contaminant, retention time, UV intensity, etc.) [2, 5, 13 - 15]. It has been concluded in a number of studies that the removal efficiency of organic contaminants is above 95%, however, the COD reduction increases to a certain extent and then declines after a certain point indicating the reactions of hydroxyl radicals with other inorganic species to form oxidizable materials [16 -17].

Phenolic complexes that are usually found in olive mill wastewater have been treated using UV/H₂O₂ method. UV/H₂O₂ has also been successfully used for removal of dyes from textile industry effluents. Various studies on textile effluent treatment show that increase in UV dosage and H₂O₂ concentration increases the rate of decolorization. Furthermore, there are a number of H₂O₂/UV industrial applications for remediation of drinking water. For example, Calgon Carbon runs two industrial AOP applications for drinking water treatment. This method is the only AOP that is used in drinking water remediation [4]

Calgon Carbon Corporation provided cost estimates for the UV/H₂O₂ system which is discussed in a study provided by Kommineni [9]. The cost shown per 3.79m³ of treated water ranged from \$0.32 for a flow rate of 1380m³/h, at 20 µg/L pollutant concentration, and \$4.11 at 13.8m³/h with 2,000 µg/L pollutant concentration. Their system had the lowest capital costs, but O&M expenditures were more due to higher energy utilisation [9].

2.3. AOP using Fenton's Reagent, Fenton-Like and Photo Fenton Processes

Radicals are produced when iron (II) reacts with hydrogen peroxide, where Fe²⁺ ion acts as a catalyst for this reaction. Fenton's Process is a simple method to produce HO• without the need for neither special apparatus nor chemicals, and takes place at ambient temperature and pressure. This method is an attractive way for oxidation, as hydrogen peroxide and iron salts are easily available, easy to handle and environmentally safe. The destruction of organic compounds takes places by reacting with the HO•. Equation 7 shows how the HO• are formed [6]:



The rate of degradation of organic pollutants with Fenton–Fenton like reagents is strongly accelerated by irradiation with UV-VIS light at wavelengths greater than 300nm. The photolysis of Fe³⁺ complexes allows Fe²⁺ to be regenerated. The occurrence of Fenton reactions in the presence of hydrogen peroxide is shown in equation 8 [15].



This process, like the other AOPs, is initiated by the hydroxyl radical for the degradation of organic compounds, mainly by oxidation reactions. However, the Fenton process is strict and requires pH control [2, 14], so as to prevent precipitation of the iron. For this method, the reactor must be constructed so as to allow proper mixing of the Fe(II) and H₂O₂. This allows for optimum hydroxyl radical formation, and degradation of the contaminants. The extraction of iron from the effluent water could possibly raise the costs of using this system.

For Fenton-like processes, elements with several redox states such as chromium, copper, and can be used to decompose H₂O₂ into HO• through conventional ways [2]. However, the Fenton-like system, each non-ferrous catalyst could counterbalance the practical gains of better catalyst stability and working at neutral pH. Therefore, the activation process for H₂O₂ is specific to the nature of the catalyst and is influenced by its composition.

Toxic compounds such as phenols and herbicides in wastewater can be destroyed by this method [6]. However, the low pH value that is required for this system to keep the iron in solution increases the maintenance and operation costs. Advanced oxidation pre-treatment using Fenton reagent has been found to be very effective at enhancing the biodegradability of wastewater containing surfactants. The Fenton, photo-Fenton and Fenton-Like methods are popular methods for AOP due to their flexibility, simplicity, and integration into existing water remediation processes such as coagulation.

Furthermore, this method has a rapid reaction between iron and H₂O₂, which then generates HO• in the shortest time compared to other AOPs [2].

The optimum amount of H₂O₂ for this process needs to be determined since any excess H₂O₂ reacts with other inorganic matter, affecting the COD reduction. This method has high elimination for the degradation of linear alkylbenzene sulfonates (LAS), and alkyl benzene sulfonate (ABS) surfactants.

However, there is one major drawback of using the Fenton process, which is the production of sludge that contains iron hydroxide as a byproduct. Large amounts of flocs of various sizes have been observed during a number of studies conducted [2, 18]. The disposal of the sludge formed has to be included when estimating the cost of this process. Nevertheless, chemical coagulation has been found as an effective method for the removal of the flocs, as well as COD [16, 19].

Until now, Fenton and photo Fenton processes have been used to treat effluents from dye and chemical manufacturing, pulp bleaching, and agricultural processing. Additionally, Fenton pretreatment can be used to enhance biological wastewater treatment. Since this process is deemed as easy-to-handle, Fenton's reaction has demonstrated to be more efficient in terms of operating expenses for the treatment of toxic and food industrial wastewater [20].

In a study of the degradation of phenol from aqueous solutions by photo-Fenton process by Alam *et al.* [21] optimum economic condition was found by using 30 mmol/L of H₂O₂ and 0.5 g/L of FeSO₄·7H₂O for irradiation time of 60 min. The total estimated costs with maximum degradation were found to be \$2.88 US/m³.

2.4. AOP using titanium dioxide (TiO₂)

Heterogeneous photocatalysis using titanium dioxide (TiO₂) is an efficient advanced oxidation method in industrial effluent treatment process. When the TiO₂ is illuminated by UV, it generates a conduction band of electrons (ecb) and valence band holes (h⁺) (Eq. 9-11). These band electrons interact with surface adsorbed oxygen to produce superoxide radical anions. The hydroxyl radicals are produced when the band holes interact with water.



It has been shown that many organic complexes can be degraded by oxidation in the presence of UV/TiO₂ [20, 22, 23]. As with all the other processes in AOP, the degradation of organic compounds takes place by reacting with the hydroxyl radicals.

Furthermore, TiO₂ nanoparticles are deemed suitable for wastewater treatment, because they are non-toxic, chemically and biologically inert, and inexpensive [4]. In addition, TiO₂ has a comparatively high oxidative power as compared to other oxidizing species [22]. Suspended TiO₂ particles were used in most studies that pertain to the photocatalytic oxidation of contaminants [23 – 25]. However, the recycling and recovery of these nanoparticles become cumbersome and expensive, thus making it a disadvantage of using suspended systems. This results in the need for composing new methods for using immobilized TiO₂ to create systems with an immobilized active phase [22, 26 - 27]. Therefore, different techniques to create immobilized TiO₂ have been studied using white plaster cement for the photodegradation of surfactants present in produced water [27].

Since photocatalytic oxidation is considered as an emerging technology, there aren't many industrial applications of the process. However, several studies show the photocatalytic process has been successfully used in the treatment of effluents from winery and distillery, olive mill, dairy industry, molasses, candy and sugar industry, fresh-cut vegetable industry, etc [20]. Photocatalysis was found to be effective for reducing counts of bacteria, molds, and yeasts.

Hydroxyl Systems Incorporated stipulated the costs for TiO₂/UV AOP system, in the study conducted by Kommineni *et al.* [9]. The estimated costs per 3.79m³ of treated water range between

\$1.01 for a flow 1380m³/h at 20 µg/L contaminant concentration and \$5.17 for 13.8m³/h at 2,000 µg/L. Compared to the other processes, this system appears to be the least cost effective.

3. Cost estimation

The expenses for AOPs greatly rely on the quality of the effluent to be treated and the aim of the treatment. Hence, there are very few reports on the cost estimation of the different types of AOPs. According to some of the studies that include cost analysis, it is recommended to carry out pilot testing to ascertain site specific costs.

It was found that the main factors influencing the prices were the removal efficiency and flow-rate, not owing to the concentration of the influent [4, 9, 18, 28]. The operating and management costs, as well as the capital costs, increased considerably with higher removal efficiency [4, 9]. Location of the plant, the time requirement for treatment, environmental trepidations and community influences should also be taken into account when evaluating the cost.

For this cost estimation, we have followed Kommineni's [9] cost evaluation guidelines. The cost estimation has been adjusted to the current year, with minimum 3% inflation rate. Out of the four cost estimations shown in Kommineni's study, Applied Process Technology provided the most cost effective rates for Capital expenditure (CAPEX) and operating expenditure (OPEX) combined for each process. Their H₂O₂/O₃ system per 3.79m³ of water, costs between \$0.35 and \$3.62 for 1380m³/h (20 µg/L), and 13.8m³/h (2000 µg/L) respectively to be treated.

In their study, Kommineni compared costs of the various AOPs based on the cost estimates. Each study was provided with a number of treatment conditions. The budget included prices for equipment, electricity, chemical quantities and spare parts. The budgets were prepared for given influent water characteristics, as shown in Table 4.

Table 4. Influent water characteristics [9]

Parameters	Value
Hardness (mg/L as CaCO ₃)	200
Alkalinity (mg/L as CaCO ₃)	250
Bromide	ND
Iron (mg/L)	<1
pH	7.0
Temperature (°F)	65
TDS (mg/L)	500
Nitrate (mg/L as NO ₃)	25
(mg/L as N)	5

The costs were divided into three categories, which are capital, operational, and O&M. The investment costs contain the full treatment system and its setting up. Under the capital cost, each of the installing costs were calculated. Valves, Piping, and electrical work were approximated at 30%, site work at 10%, engineering at 15% and contractors at 15% of the equipment costs. In addition, 20% of the overall cost was included as a contingency. Amortization of the annual capital cost was based on a 30-year period, at a discount rate of 7%. The full illustration of the calculation is shown in Table 5.

Table 5: Cost estimation for AOP Unit [9]

Item	Costs (USD)
Advanced oxidation unit	1,200,000
Piping, valves, electrical (30%)	360,000
Site work (10%)	120,000
Contractor O&P (15%)	252,000
Engineering (15%)	289,800
Contingency (20%)	444,360
TOTAL CAPITAL	2,666,160
Amortized capital	214,864
Annual O&M	207,507
Total annual cost	422,371
Total cost per 1,000 gallons treated	1.34

For the annual OPEX, replacement expenses are based on the estimate of 1.5% capital cost. The labour costs will vary for different countries. Analytical costs are based on the number of sampling conducted per week. The chemical costs will be based on dosages. Power is based on estimated consumption and price per unit for the country of operation.

In a study conducted by Mahmuni et. al [28], a method to estimate treatment costs of various AOPs was developed. Kinetic data of pollution removal from various literature were used for their estimation. The rate constants for the kinetic data were then used to estimate the time it takes for degradation of the pollutant by 90% of its original concentration. This time was taken to be the residence time of the reactor. The residence time was then multiplied with the design flowrate to calculate the reactor capacity. Total energy requirement in the AOP reactor was calculated, and this used to find the estimated cost of the AOP reactor.

4. Conclusions and ways forward

Advanced oxidation process is gaining popularity in the wastewater treatment industry. The main focus of this process is the hydroxyl radical, which once generated aggressively attacks virtually all organic compounds. Thus far, photocatalytic (TiO₂/UV) process, ozonation, H₂O₂/UV process and Fenton's reactions have been studied and extensively used for the removal of recalcitrant organic chemicals thus reducing the COD, TOC, dyes, and phenolic compounds that are commonly found in industrial and municipal wastewater. Major factors affecting these processes are the initial concentration of the pollutant, the quantity of oxidizing agents and catalysts, light intensity, irradiation time and the nature of the wastewater's solution (pH, presence of solids and other ions). It is pertinent to conduct experimental studies in order to develop a method suitable for the specific wastewater. It has been established that it is necessary to estimate the capital costs, and overhead and management costs by conducting pilot studies, since pilot plant studies are better capable of providing closer conditions to estimate accurate costs. Based on the limited reviews, H₂O₂/O₃ and H₂O₂/UV appear to be the two most promising AOP systems, and they are economically practical.

Few AOPs have been examined in detail under controlled experimental conditions, for many it is uncertain what the exact chemical mechanisms are, and few field tests have been carried out in such a

manner that the entire process could be critically examined. Hence, process optimization should be carried out for specific wastewater, to ensure no harmful by-products are generated, and residual reagents are limited in the effluent from the AOP system. At the same time the knowledge about the exact mechanisms of AOPs is still incomplete. Furthermore, one should clearly see the importance of AOPs as a technological tool for environmental management, and they must be developed from this firm scientific and engineering basis.

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