

## AN OVERVIEW OF THE INTEGRATION OF ADVANCED OXIDATION TECHNOLOGIES AND OTHER PROCESSES FOR WATER AND WASTEWATER TREATMENT

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### ABSTRACT

Integration of advanced oxidation technologies and other traditional wastewater treatment processes has been proven to be more effective for treating polluted sources of drinking water and industrial wastewater economically. The way of selecting the methods depends on the characteristics of the waste stream, environmental regulations, and cost. Reviewing the experimental works on this area and discussing their effectiveness as well as modeling would be helpful for deciding whether the integrated processes is effective to fulfill the annually restricted legislations with lower investment. Therefore, optimization of each process should be done based on different aspects such as operation time, operating cost, and energy consumption. In this review, recent achievements, developments and trends (2003-2009) on the integration of advanced oxidation technologies and other remediation methods have been studied.

**Keywords:** Advanced oxidation technologies, Biological processes, Physical methods, Integration of Processes, Optimization

## 1. INTRODUCTION

In recent decades, very severe regulations have forced researchers to develop and evolve novel technologies to accomplish higher mineralization rate with lower amount of detectable contaminants. Different physical, chemical, and biological treatment processes have been employed to treat various municipal and industrial wastewaters such as chemical [1-2], biological, food [3], pharmaceutical [4-5], pulp and paper [6], dye processing and textile [7-10], and landfill leachate [11] effluents. These processes are also being used for oxidizing, removing, and mineralizing various surface and ground waters. The waste streams contain a wide range of compounds with different concentrations. Based on the concentrations and the type of contaminants exist in the wastewater, various treatment methods have been developed to release an environmentally friendly effluent. Pollutants can be classified in several categories. Decision making can be based on whether the chemicals are organic or inorganic and they can be branched out based on chemical structure, solubility, biodegradability, volatility, toxicity, polarity, oxidation potential, adsorbability, electrical charge, and the nature of daughter compounds. Studies on the wastewater treatment area have been conducted in two main groups: treatment of single and multi-component solutions. Although results obtained by single component solutions are more helpful for predicting the behavior of such solutions, wastewater streams containing a single compound are very rare and the results cannot be applicable to actual wastes. On the other hand, studies on multi-component solutions are useful to employ for real wastewater streams in larger scale. In investigating multi-component systems, some problems such as daughter compounds' formation during oxidization, inter-reaction between existing compounds besides difficulty of modeling and simulation of such systems make experimentation very complicated.

Some researchers prefer to study the actual effluent from various industries but others prefer to investigate synthetic wastewater behavior. Both have their own advantages and drawbacks. Synthetic wastewater is helpful in a way one can measure intermediates during the degradation and mineralization. Moreover, these kinds of experiments can be extended for a range of different concentrations for each compound. On the other hand, actual waste solution from a specific source is beneficial to solve the problem of a real case. As explained earlier, choosing the best method of remediation depends on the characteristics and concentrations of different compounds in a wastewater. For example, physical treatment processes are very effective to separate volatile organic compounds (VOCs) using a gas stripper column. For real effluents, sometimes employing different techniques is more beneficial to separate, degrade, and mineralize various components of different behavior. In the case of municipal and industrial wastewater treatment plant, different processes such as physical, chemical, and biological are being used to increase the efficiency. Deciding about the selection of treatment methods is also influenced by the intermediates produced during oxidization (the product of previous process). The entity of the chemicals after each chemical processes are normally changed due to chemical reactions occurred. Therefore, the selection, design, and operation of such processes and their post-treatment methods should be carefully carried out. The responsibility of chemical treatment techniques has the governing role in facilitating the remediation. Chemical processes can change the characteristics of chemicals such as toxicity and biodegradability. Therefore, suitable techniques should be opted for further cleaning of the new product.

Among chemical technologies, a novel method that has been growing in recent decades is the advanced oxidation processes (AOPs) which are very potent in oxidization, decolorization, mineralization, and degradation of organic pollutants. Due to high oxidation rate of the chemical reactions caused by AOPs, the behavior of chemicals is significantly changed after the treatment. The degradation makes organic chemicals smaller and biodegradable. AOPs for wastewater treatment are not an economical process due to their high operating cost, thus; it is suggested to integrate these technologies with other post-treatment methods such as biological processes. The integration of advanced oxidation technologies and biological processes has been reviewed by Scott and Ollis (1995) [12], Tabrizi and Mehrvar (2004) [13], and Mantzavinos and Psillakis (2004) [14]. The aim of this study is to review and analyze recent studies on

the integration of AOPs and other conventional techniques for the treatment of water and wastewater during the period of 2003 to 2009.

## 2. ADVANCED OXIDATION PROCESSES

In the past two decades, advanced oxidation processes (AOPs) have been proven to be powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants [15]. These technologies could be applied for contaminated groundwater, surface water, and wastewaters containing recalcitrant, inhibitory, and toxic compounds with low biodegradability as well as for the purification and disinfection of drinking water. Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical ( $\cdot\text{OH}$ ) generation as the primary oxidant (second highest powerful oxidant after the fluorine). These radicals are produced by means of oxidizing agent such as  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts. Investigators are trying to find better methods for  $\cdot\text{OH}$  production. Hydroxyl radicals are non-selective in nature and they can react without any other additives with a wide range of contaminants whose rate constants are usually in the order of  $10^6$  to  $10^9 \text{ mol.L}^{-1}.\text{s}^{-1}$  [16-17]. These hydroxyl radicals attack organic molecules by either abstracting a hydrogen atom or adding hydrogen atom to the double bonds. It makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization. A full understanding of the kinetics and mechanisms of all the chemical and photochemical reactions involved under the condition of use are necessary, by which, based on the well understood mechanisms, optimal conditions could be obtained.

The most eye-catching drawback of advanced oxidation technologies is their operating cost compared to other conventional physicochemical or biological treatments. Therefore, AOPs cannot achieve complete mineralization due to this restriction. One of the most reasonable solutions to this problem is coupling AOPs with other treatment methods. Advanced oxidation processes often are employed as a pre-treatment method in an integrated system. AOPs are also able to enhance the biodegradability of contaminants through converting recalcitrant contaminants into smaller and consequently more biodegradable intermediates. This integration is justified commercially when intermediates are easily degradable in the next process. There are some review papers on the integration of chemical and biological treatment processes [12-13, 17]. In this study, recent achievements and developments on the integrations of AOPs and other treatment methods during the period of 2003-2009 are provided. Table 1 shows the main results along with the operating conditions obtained by the recent studies. The selection of the method, the equipment, the operating conditions, and the sequence of the processes are better obtainable based on the recent achievements.

Table 1: Summary of recent studies on the Integration of AOPs with other processes for water and wastewater treatment

Target Compound(s)	System and Method	Efficiency	References
Surfactant effluent containing abundant sulfate ions	Initial COD: 1500 and 490 mgL <sup>-1</sup> , Lab scale Fenton process effluent concentrations were 230 and 23 mg L <sup>-1</sup> after 40 min. In pilot scale Fenton followed by immobilized biomass reactor was employed.	40 min for Fenton process and 2 h for biological treatment were sufficient to reduce the effluent concentration up to less than 100 and 5 mgL <sup>-1</sup> for COD and LAS concentration. The effect of ferrous ions is more important than that of H <sub>2</sub> O <sub>2</sub> . Sufficient dosage of Fe <sup>+2</sup> was 600 mgL <sup>-1</sup> for an efficient treatment. Increasing the H <sub>2</sub> O <sub>2</sub> leads to higher biodegradability.	18
Pulp and paper	2 different samples with 2500 and 3520 mgL <sup>-1</sup> COD, were treated by some chemicals (alum, lime and polyelectrolyte) up to 1900 mgL <sup>-1</sup> , Followed by activated sludge process up to 260-400 mgL <sup>-1</sup> , then secondary wastewater was treated by different methods such as ozonation, catalytic ozonation, H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> , and Fenton.	The removal efficient of secondary wastewater was arranging: Fenton > H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> > Ozonation > catalytic ozonation with metal oxides. In ozonation: for higher COD, 60% COD reduction was observed after 1 h. No further degradation was found after 2 h. For lower COD in less than 30 min, 200 mgL <sup>-1</sup> effluent was obtained. Fenton process showed 88% and 50% COD reduction for secondary and raw wastewater. Optimum chemicals concentration ratios were 0.5 mol/1 mol Fe <sup>+2</sup> /H <sub>2</sub> O <sub>2</sub> and 2 mol/1 mol H <sub>2</sub> O <sub>2</sub> /COD.	19
Landfill leachate	Wastewater pretreated by sequence batch reactor was used for additional advanced oxidation such as O <sub>3</sub> , O <sub>3</sub> /pH adjustment (pH 9), H <sub>2</sub> O <sub>2</sub> , O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> and performic acid	After 2h pretreatment with activated sludge, ozone and pH adjusted ozone showed the highest biodegradability. The most efficient method was observed in combination of O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> and biological treatment as pre- and post-treatment. Performic acid did not show any TOC reduction.	20
2,4,5-trichlorophenol	122 ml bench scale photocatalytic circulating-bed biofilm reactor (PCBBR), high intensity UV lamp and Degussa P25 TiO <sub>2</sub> were used for irradiation source and photocatalyst,	UV photocatalysis alone did not show any degradation up to 96 h, After the addition of carriers with biofilm, biodegradation of acetate was started quickly up to 200h and then smooth acetate concentration was observed.	21

respectively

Hydroxyl-benzene	Photo-Fenton process in a 8 L 6-lamp CPC solar continuous photoreactor for treating raw river water and pretreated with slow sand filtration river water	Photolysis (with H <sub>2</sub> O <sub>2</sub> and without Fe <sup>+3</sup> ) showed 57% and 65% TOC reduction before and after SFF. Fe <sup>+3</sup> concentration even as low as 1 mgL <sup>-1</sup> depicted treatment improvement drastically. The presence of H <sub>2</sub> O <sub>2</sub> under sunlight resulted in 50% mineralization.	22
Cibacron Red FN-R	A two stage aerobic-anaerobic method followed by photo-Fenton and ozonation processes was employed. The initial concentration of wastewater samples were 250, 1250, 3135 mgL <sup>-1</sup> .	Aerobic treatment showed less than 9% biodegradation after 28 days. The photo-Fenton process conducted with different ratios of Fe <sup>+3</sup> /H <sub>2</sub> O <sub>2</sub> , 10/250, 20/500, and 100/2500 mgL <sup>-1</sup> /mgL <sup>-1</sup> . DOC reduction was increased with increasing of Fe <sup>+3</sup> and H <sub>2</sub> O <sub>2</sub> . After 30 min, DOC was reached a plateau and no further DOC removal was observed. Ozonation was carried out with different pH (3, 7, 10, and 10.5). pH 10.5 showed the best results (83% mineralization in 150 min). Neutral and acidic ozonation showed 48% degradation.	23
Phenol	Hydrodynamic cavitation combined with advanced Fenton was employed for treating phenolic wastewater (2.5 mM).Hydrodynamic cavitation was generated by a liquid whistle reactor (LWR).	Results showed that both hydrodynamic cavitation and advanced Fenton have greater efficiency for lower phenol concentration. Continuous leaching resulted in higher concentration of iron ions with longer residence time. Increasing H <sub>2</sub> O <sub>2</sub> dose in the range of 500-2000 mg/L led to greater TOC removal. In hydrodynamic cavitation, applied pressure had positive effect on TOC reduction. The closer distance between orifice and catalyst bed also performed better TOC removal.	24
Nonylphenol (NP)	Sonochemical reactor equipped with 300kHz ultrasound transducer and cooling system, combined with biosorption of fungal cultures was used for treating different	US-Fenton process showed better degradation rate in case of lower initial contaminant concentration. Lowest initial concentration performed the complete mineralization. On the other hand, US only and Fenton only were ineffective after 1-2 h. Biosorption showed	25

	concentrations (100, 500, and 1000 ppm) of polluted water.	around 39 and 60% removal after 4 and 7 days. Initial concentration did not affect the removal percentage. In combined method 74 and 88% NP removal were observed after 1h US/Fenton and subsequent 4 and 7 days biosorption, respectively.	
Methomyl, Dimethoate, Oxamyl, Cymoxanil, Pyrimethanil	50 mgL <sup>-1</sup> concentration of each compound was used to be treated in combined AOP/biological method. AOPs were TiO <sub>2</sub> photocatalysis and photo-Fenton. 35 L solar pilot plant equipped with 3 CPCs for TiO <sub>2</sub> photocatalysis and 75 L solar pilot plant using 4 CPCs were employed for AOP stage. A 35 L aerobic immobilized biomass reactor (IBR) was used for biological treatment.	90% DOC removal was observed in 1197 and 512 min in case of case of TiO <sub>2</sub> photocatalysis and photo-Fenton. Shorter irradiation time with two different iron concentrations (20 and 55 mgL <sup>-1</sup> ) resulted in 50 and 72% DOC reduction. Photo-Fenton process showed greater pesticide degradation (more than twice) than the TiO <sub>2</sub> photocatalysis. Pretreatment by photo-Fenton process decreased toxicity from 90 to 47%. Biodegradability tests showed 70% biodegradability is obtained after 12 days. Combined batch method showed 85% efficiency (23% AOP, 62% biological treatment). Combined batch AOP and continuous biological treatment showed more than 90% removal.	26
Procion blue	A 130 ml plate and frame electrochemical flow cell and immobilized photocatalytic UV reactor were employed for degradation of 50 mg/L procion blue solution	Photo-electrochemical and photocatalytic electrochemical methods showed 98% dye degradation within 7 h. After 4 h different combined method showed more than 90% color removal. COD removal was proportional to applied current. The optimum TiO <sub>2</sub> concentration was 40 mgL <sup>-1</sup> . Acidic condition performed greater degradation.	27-28
Reactive black 5 (RB5), Reactive blue 13 (RB13), Acid orange 7 (AO7)	Fenton processes followed by aerobic biological treatment (sequential batch reactors) were used for 50 mg/L dye solution. Different factors such as pH, H <sub>2</sub> O <sub>2</sub> and Fe <sup>+2</sup> were optimized.	pH 3 showed the highest decolorization for all dyes (more than 99%), Decolorization was increased at higher H <sub>2</sub> O <sub>2</sub> concentration up to an optimal dose(50 mgL <sup>-1</sup> ). optimal Fe <sup>+2</sup> dose was found to be 15 mgL <sup>-1</sup> . 82, 89, and 84% COD removal was observed for RB5, RB13, and AO7, respectively.	29
Pharmaceutical	The combination of solar AOP	Industrial effluent containing α-methylphenylglycine	30

factory effluent	followed by biological treatment. Four CPC with 1.04 m <sup>2</sup> with 50 mm diameter absorber tubes. Initial TOC was 500 mgL <sup>-1</sup> . Iron concentration was 20 mgL <sup>-1</sup> .	(MPG) treated using a pilot plant. Fenton (Fe <sup>+2</sup> = 20 mgL <sup>-1</sup> ) process showed complete degradation and 70% TOC reduction in less than 1 h with seawater, but in case of distilled water, the degradation rate was 3 times greater. 60 mM of H <sub>2</sub> O <sub>2</sub> is required to degrade MPG. For complete MPG degradation, 30-35 mM H <sub>2</sub> O <sub>2</sub> is required and also for cost minimization, the H <sub>2</sub> O <sub>2</sub> concentration should be kept around 150 mgL <sup>-1</sup> . Batch mode treatment in immobilized biomass reactor (IBR) showed 80% TOC reduction for pre-treated water after 4-5 days. 150 min illumination is required to reach the biodegradability threshold. In industrial scale, 100 m <sup>2</sup> CPC collectors are sufficient to treat 3 m <sup>3</sup> /day wastewater.	
Textile surfactant formulation	UV/H <sub>2</sub> O <sub>2</sub> using 40 W low pressure mercury vapor lamp carried out with different pH (from 5 to 12) and H <sub>2</sub> O <sub>2</sub> dose from 10-100 mM for treating textile surfactant formulation with an initial 1000 mgL <sup>-1</sup> COD.	pH did not show significant influence on the AOP mechanism but the pH was decreased until neutral condition due to formation of the acids during degradation. The optimal H <sub>2</sub> O <sub>2</sub> dose was found to be 917 mgL <sup>-1</sup> . Biodegradable COD was increased from 4 to 14-15% when the UV/H <sub>2</sub> O <sub>2</sub> (60 mM H <sub>2</sub> O <sub>2</sub> and 60-90 min illumination time) was used as a pretreatment. Rapidly hydrolysable COD significantly increased during photochemical treatment but against results were found for slowly hydrolysable COD.	31-32
Distillery wastewater	The distillery spent wash was pre-treated by thermal and sonication (ultrasonic bath) and ozonation (flow rate: 260 l/h) processes sent to biological treatment process.	Ultrasonic (US) pretreatment did not show significant COD (13% after 48 h), decolorization, and TOC reduction but converted complex organic compounds into smaller ones. Ozonation was effective on the decolorization and COD reduction (45.6%) and the pH was decreased 0.1-0.2 units every 2 min. Oxidizing and mineralization rate was enhanced with an increase of ozone flow rate. Ozonation pretreatment resulted in greater biodegradability enhancement than US.	33-34

Diuron and Linuron	42 mgL <sup>-1</sup> Diuron and 75 mgL <sup>-1</sup> Linuron was chosen for the photo-Fenton and biological treatment. Different doses of H <sub>2</sub> O <sub>2</sub> (97.1, 143, and 202 mgL <sup>-1</sup> ) and Fe <sup>+2</sup> (9.25, 13.3, and 15.9 mgL <sup>-1</sup> ) were used for photo-Fenton process.	TOC reduction was significantly enhanced by an increase of Fe <sup>+2</sup> and H <sub>2</sub> O <sub>2</sub> doses. Inorganic acids such as acetic acid, oxalic acid, and formic acid were produced, reached a maximum and then degraded during photo-Fenton process, higher dose of H <sub>2</sub> O <sub>2</sub> and Fe <sup>+2</sup> resulted in greater production and degradation rate.	35-36
Natural water systems	Enhanced coagulation (using alum and ferric chloride) and photocatalytic oxidation (UV/TiO <sub>2</sub> ) were employed to treat three different natural water samples.	Ferric chloride coagulation showed better coagulation compared with alum.	37-38
Reactive black 5 (RB5)	Fenton process in 800 ml cylindrical glass reactor was combined with yeast as a post treatment was employed to degrade 100-200-300-500 mgL <sup>-1</sup> RB5. The Fe <sup>+2</sup> /H <sub>2</sub> O <sub>2</sub> ratio was 10.	Decolorization rate was significantly decreased with an increase of RB5 concentration so that after 60 min, 98 and 62.6% decolorization was observed for 100 and 500 mgL <sup>-1</sup> samples. For solution concentration greater than 200 mg <sup>-1</sup> incomplete decolorization was observed. The reaction rate constant for 100 mgL <sup>-1</sup> solution was 10 times greater than that of 500 mgL <sup>-1</sup> but the half-life was 0.01 of the latter solution. Decolorization under yeast experiment was not able to completely decolorize concentration greater than 200 mgL <sup>-1</sup> . The impact of initial concentration in biological treatment was lower. The combined method showed complete decolorization of 500 mgL <sup>-1</sup> solution.	39
Natural organic matter (NOM)	Combined UV/H <sub>2</sub> O <sub>2</sub> (equipped with LP lamp) and biological activated carbon (BAC) in a 2 cm diameter column used for degradation of NOM.	Disinfection by product formation potential (DBP-FP) was effectively removed during UV/H <sub>2</sub> O <sub>2</sub> at higher UV fluency, but AOP-BAC showed significant organic carbon content reduction. During AOP the concentration of dichloroacetic acid (DCAA) increased	40

		<p>due to formation of some intermediates such as aldehydes but in subsequent BAC, DCAA concentration was significantly decreased. Trihalomethane formation potential (THM-FP) and trichloroacetic acid formation potential (TCAA-FP) also showed no change or slight reduction in AOP, and great removal was observed during integrated AOP-BAC.</p>	
Resin acids (abietic acid, dehydroabietic acid, isopimaric acid)	Different AOPs such as ozonation, O <sub>3</sub> /UV, O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> in a 1.5 L photoreactor combined with activated sludge were used.	The highest COD reduction was observed under O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> @ T=80°C. Higher temperature resulted in lower required ozone for degradation. Dehydroabietic acid showed greater resistance to be oxidized by ozone. Biological post-treatment indicated that the biodegradability of resin acids was decreased during AOP because of the production of more resistant byproducts.	41
Reactive red 195A (RR195A)	Combined UV/H <sub>2</sub> O <sub>2</sub> and moving bed biological reactor was used for treatment the experimental design was based on H <sub>2</sub> O <sub>2</sub> dose, radiation time and circulation ratio (0 to 600%).	The optimization was carried using Box-Wilson statistical design method. The greatest impact was observed by recirculation ratio. In addition, higher irradiation time and H <sub>2</sub> O <sub>2</sub> dose were effective for better decolorization.	42
Tetrahydrofuran (THF), 1,4-dioxane, pyridine	Biodegradability of the compounds individually and mixed was analyzed after UV/H <sub>2</sub> O <sub>2</sub> and UV/O <sub>3</sub>	UV/H <sub>2</sub> O <sub>2</sub> showed greater efficiency for increasing biodegradability and destruction than UV/O <sub>3</sub> for treating THF solution. For dioxane solution UV/H <sub>2</sub> O <sub>2</sub> degraded all the contaminants within 60 min but did not show biodegradability improvement. No biodegradability enhancement was observed during UV/O <sub>3</sub> and UV/H <sub>2</sub> O <sub>2</sub> of pyridine. UV/O <sub>3</sub> slightly improved the biodegradability of the mixture.	43
Deltamethrin, lambda-cyhalothrin,	100 mgL <sup>-1</sup> of three pesticides with 6500, 6300, 6500 mgL <sup>-1</sup> COD were selected for O <sub>3</sub> and O <sub>3</sub> /UV	Over 80 and 92% degradation observed under O <sub>3</sub> and O <sub>3</sub> /UV, respectively. Higher pH showed positive effect on the degradation and COD reduction. In combined	44

triadimenol	degradation alone and combined with biological treatment.	process, O <sub>3</sub> /UV pre-treated solution showed higher degradation rate as compared to O <sub>3</sub> pretreated, aerated, and raw solutions. Temperature was effective for enhancing the biodegradation.	
Pulp and paper effluent	Combined AOP (photocatalysis or ozonation) and biological process was assisted for treating Kraft E1 and black liquor effluent. TOC of these effluents were 934 and 128750 mgL <sup>-1</sup> .	Suspended photocatalysis showed a better decolorization for Kraft E1 with respect to ozonation (54 versus 27%). On the other hand, decolorization of black liquor effluent was more desirable with ozonation (14 versus 5%) due to the darkness of the solution. Photocatalysis showed 45% improvement for mineralization of Kraft E1, but ozonation enhanced 37% mineralization in combined method.	45
Green table olive processing wastewater	Lab scale and pilot scale of biological treatment followed by electrochemical reactor in the presence and absence of H <sub>2</sub> O <sub>2</sub> was studied.	Inoculum's size performed positive effect on COD removal so that 10 <sup>4</sup> and 10 <sup>6</sup> conidia ml <sup>-1</sup> showed 71.5 and 85.5% COD reduction. pH decreased faster for the high inoculum concentration. Most of the contaminants were degraded completely during biological treatment. Pre-treated solution was sent to electrolytic reactor with various H <sub>2</sub> O <sub>2</sub> dose (0, 2.5, and 5 v%). Results showed that the degradation was increased in the presence of H <sub>2</sub> O <sub>2</sub> . In pilot plant, 98% COD reduction was obtained during combined processes.	46
Dissolved organic matter (DOM) in drinking water	Single stage and multistage ozonation-biological and AOP-biological treatment were used for oxidizing DOC of the reservoir water and secondary effluent of the municipal wastewater when the DOC concentration was 20 mgL <sup>-1</sup> .	AOP-biological showed better mineralization rather than ozonation-biological. Further mineralization was achieved in multi-stage process, because in each biological stage, BDOC portion of the effluent was removed because this fraction can act as radical scavenger. Single stage and Multistage ozonation-biological did not perform significant oxidization for residence time greater than 15 min.	47

4-chlorophenol (4-CP)	Photo-Fenton in 2.2 L reactor followed by sequencing batch biofilter reactor (SBBR) was used for treating 200 ppm of 4-CP	H <sub>2</sub> O <sub>2</sub> showed higher influence on the degradation rate rather than Fe <sup>+2</sup> and temperature. Moreover, higher H <sub>2</sub> O <sub>2</sub> dose improved the biodegradability of the solution.	48
Cibacron brilliant yellow 3G-P	Combined photocatalysis (1 mgL <sup>-1</sup> TiO <sub>2</sub> ) and aerobic biological (activated sludge) treatment was used for 100 mgL <sup>-1</sup> of the target.	Higher decolorization rate was observed under aerobic treatment of partially photocatalytically pre-treated solution. Acclimated sludge also increased the oxygen uptake rate of the solution.	9-10
Winery wastewater	Solar homogeneous and heterogeneous photo-Fenton process was employed in the presence of 10 mL <sup>-1</sup> H <sub>2</sub> O <sub>2</sub> for treating winery wastewater (COD= 3300 and TOC = 969 mgCL <sup>-1</sup> )	Unlike the heterogeneous photo-Fenton, Homogeneous method required additional H <sub>2</sub> O <sub>2</sub> during the experiments. Homogeneous performed higher degradation rate and TOC reduction rather than heterogeneous photo-Fenton. The heterogeneous Fenton method was advantageous because further precipitation was not necessary.	49
Cellulose effluent	The effluent from the acid stages of the bleaching process of Eucalyptus urograndis wood was examined by activated sludge followed by UV radiation (200 ml batch reactor)	Activated sludge increased the wastewater color but it was very effective for COD and BOD reduction. UV radiation was helpful for decolorization and it showed lower ability for COD and BOD removal. The combined system did not show any improvement for further BOD and COD reduction.	50
Mixed industrial wastewater	Pathogen removal and re-growth of an UASB effluent was studied with ozonation, UV, UV/H <sub>2</sub> O <sub>2</sub> , peracetic acid (PAA)	Increasing the ozonation time did not improve the pathogen removal. 350 mgL <sup>-1</sup> H <sub>2</sub> O <sub>2</sub> , 15 V% PAA, and 120 sec UV radiation was effective for above 99% pathogen inactivation. In higher temperature (35 <sup>0</sup> C) pathogen re-growth was higher.	51
Semiconductor wastewater	Combined physical (fixed bed air stripping column), chemical (Fenton	Air stripper was used to recover isopropyl alcohol (IPA). IPA recovery was enhanced by increasing air	52

	process), and biological (sequencing batch reactor (SBR)) was employed for treating a semiconductor wastewater and recover isopropyl alcohol.	flow rate, temperature and separation time. Fenton was very effective at pH between 2 and 5. Lower $\text{FeSO}_4$ dose (lower than $5 \text{ mgL}^{-1}$ ) showed greatest COD reduction. The removal rate was also increased under higher $\text{H}_2\text{O}_2$ flow rate up to $1 \text{ ml/min}$ . Temperature was also beneficial for better Fenton efficiency. SBR with 12 cycles performed well to reduce COD from $600$ to $100 \text{ mgL}^{-1}$ .	
2,4-dichlorophenol (2,4-DCP)	100 ppm 2,4-DCP was treated in combined ozonation and biological treatment (activated sludge and acclimated biomass with phenol)	Ozonation improved the biodegradability of the solution from 0 to 0.25 and 0.48 for $\text{BOD}_5/\text{COD}$ and $\text{BOD}_{21}/\text{COD}$ . Activated sludge (non-acclimated with phenol) showed better removal rate than that of acclimated to phenol.	53
Linear alkylbenzene sulfonate (LAS)	76.6 L Pilot plant cylindrical photoreactor ( $\text{UV}/\text{H}_2\text{O}_2$ ) for 12, 25, 50, $100 \text{ mgL}^{-1}$ LAS	Biodegradability was increased during LAS photocatalysis especially for lower concentration of LAS. Over 90% of LAS was removed and biodegradability increased up to 0.4 during 90 min. Solution BOD was increased with photocatalysis residence time.	54
Methyl <i>tert</i> -butyl ether (MTBE)	3 L batch glass photoreactor equipped with 2 different UV lamps with wavelengths 365 and 254 nm employed for $\text{UV}/\text{H}_2\text{O}_2$ and $\text{UV}/\text{TiO}_2$ followed by biodegradation using SBR	Over 90% MTBE removal achieved by $\text{UV}/\text{H}_2\text{O}_2$ within 1 h. Optimal $\text{H}_2\text{O}_2$ dose was 14 times greater than MTBE dose. UV-254 was more effective than UV-365 for both $\text{UV}/\text{H}_2\text{O}_2$ and $\text{UV}/\text{TiO}_2$ in degrading MTBE. $\text{UV}/\text{H}_2\text{O}_2$ and $\text{UV}/\text{TiO}_2$ were not effective for enhancing the biodegradability of solution.	55
Wool scouring effluent	Flocculation followed by aerobic biological treatment is being used to treat and $\text{UV}/\text{H}_2\text{O}_2$ was used as a post-treatment process. Biological treatment was also used as a post-treatment process.	$\text{BOD}_5$ was increased during $\text{UV}/\text{H}_2\text{O}_2$ from $<10$ to $86 \text{ mgL}^{-1}$ . COD and TOC were removed by 75 and 85%, respectively. Decolorization was complete in less than 30 min. pH variation was ineffective on COD and TOC reduction. Higher COD removal was achieved in integrated AOP and Biological post-treatment.	56

Oily wastewater from the lubricant unit

UV/H<sub>2</sub>O<sub>2</sub> followed by biological (*Pseudomonas putida* DSM 437) treatment used to treat oily wastewater containing ethylene glycol, phenol, *p*-cresol, *o*-cresol. Direct biological results were compared to integrated system

Biodegradation alone showed 60% COD reduction. Fe<sup>+3</sup>/UV/H<sub>2</sub>O<sub>2</sub> improved COD reduction rather than UV/H<sub>2</sub>O<sub>2</sub> from 5 to 30% within 10 min. Integrated photolysis and biological showed greater organics removal relative to direct biodegradation. For example ethylene glycol was 100% removed from the solution. COD removal was increased from 60 to 72% by integrated process.

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### 3. PHYSICAL PROCESSES

Physical processes are widely used in the water and wastewater treatment plants. These physical techniques are based on the separation of one or more compounds from the waste stream. Because of the separation, the pollutant is transferred from one phase to another. Therefore, further treatment is required for the degradation of the contaminants in the second phase. Physical methods are employed mainly to separate large settleable and floating matter, clarify turbid solutions, recover and recycle valuable substances utilized in the main processes and separating inorganic materials. The conventional and advanced physical techniques include filtration, adsorption, gas stripping, and others. Physical treatment methods can be used before or after the advanced oxidation processes depending on the influent nature and its concentration as well as the AOPs operation conditions. Using physical techniques in wastewater treatment before and after the AOPs can be selected based on the consideration of various aspects of applications provided as follow: It is believed that the insoluble compounds and solid matter should be removed before any chemical or biochemical treatment because these materials may damage the equipment, increase the size of the equipment, results in a greater cost, and reduce the process efficiency.

For AOPs utilizing an irradiation source such as UV lamps (UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/TiO<sub>2</sub>, photo-Fenton and others), turbid solutions reduce the efficiency of the system. Turbidity decreases the local volumetric rate of energy absorption (LVREA) in the photoreactor, thus, the attenuation coefficient inside the reactor increases and it leads to smaller photochemically effective radiation field. Therefore, it is required to reduce the turbidity of the solutions by means of physical methods. The presence of some compounds in the solution that can adsorb on the surface of the catalyst results in deactivation of the catalyst due to the occupation of active sites. The lower amount of valent sites decreases the mass transfer between the catalyst and the species exist in the reactor, therefore, it reduces the number of hydroxyl radicals generated in the system. Some substances can also increase the agglomeration and aggregation of the catalyst powders in the system and reduce the mass transfer rate and system efficiency.

Free radical scavengers such as carbonate and bicarbonate ions reduce the number of hydroxyl radicals and system efficiency. Furthermore, these ions increase the attenuation coefficient and reduce the irradiation field. Physical and chemical methods can be employed for reducing such ions. Inorganic compounds such as heavy metals along with some chemicals may be detrimental to the AOPs and other subsequent processes. Therefore, they should be removed before AOPs. These substances are generally removed by adsorption, biosorption, and partition [58] methods such as granular activated carbon (GAC) column [59], biological activated carbon (BAC) column [60], unmodified clays (kaolinite and smectite) organoclays modified with short and long chain organic cations [61], or natural and modified zeolite [62].

It is beneficial to remove some compounds that have relatively lower oxidation potential than other compounds in the wastewater solutions by low cost physical methods. The separation of such compounds can help to keep the concentration of hydroxyl radicals high enough. The separation of volatile organic compounds is also helpful before ultrasonic AOPs. The oxidation of volatile organic compounds by acoustic cavitation is usually conducted by combustive reactions due to their extremely high temperature and pressure. If these compounds are removed before advanced oxidation processes, a lower power and ultrasonic intensity are required to oxidize the wastewater.

As mentioned earlier, AOPs change the characteristics and entity of the chemicals during the process, therefore, sometimes it is beneficial to use physical post-treatment. For example, the effluent of the AOPs may be adsorbed better by GAC. The most important issues in designing integrated processes such as fixed and operating costs should not be disregarded in order to achieve the desirable concentration limit of compounds.

### 4. BIOLOGICAL TREATMENT

Biological treatment methods are very common in wastewater treatment plants. These processes are useful for treating biodegradable waste streams. The use of biological treatment is attractive due to its low

operating cost but the residence time is very high relative to that of other processes. On the other hand, the removal rate of advanced oxidation processes is relatively high while the operating cost is relatively expensive due to the use of reagents and irradiation sources. Capital and operating costs of biological treatment methods are 5-20 and 3-10 times cheaper than those of chemical methods, respectively [56-63]. Based on the cheaper construction and their operating cost, it is desirable to maximize the residence time and the removal rates of contaminants in biological processes. Biological treatment techniques are classified into two main groups: aerobic and anaerobic. Aerobic processes could be carried out by suspended (activated sludge), attached (biofilm reactor, trickling filter, and rotating disk contactor) or combined (moving bed biofilm reactor) depending on the operating conditions and wastewater characteristics. Wastewater can also be treated by anaerobic processes such as up-flow anaerobic sludge blanket (UASB), anaerobic fluidized bed reactor (AFBR), expanded granular sludge bed (EGSB), and anaerobic baffled reactor (ABR). Anaerobic techniques are usually employed for treating a concentrated municipal and industrial wastewater.

Depending on the type of wastewater, the nature of compounds and their concentrations, the integration of AOPs and biological processes could be designed in different configurations as follows: Wastewater solutions containing compounds which are toxic and inhibitory to biomass are necessary to be pre-treated by advanced oxidation processes. The AOPs reduce the toxicity of the wastewater. AOPs are also beneficial to pre-treat the wastewater containing bio-recalcitrant substances. This kind of wastewater is not biodegradable enough to be treated by biological processes. If the ratio of the BOD/COD of a wastewater is lower than 0.4, it is categorized as non-biodegradable or low in biodegradability [10,13]. Most AOPs enhance the biodegradability of the wastewater usually by decreasing the COD load. A class of waste solutions and wastewater streams is categorized as a biodegradable wastes with small amounts of recalcitrant compounds. This group contains a wide range of domestic and industrial effluents because none of the effluents after preliminary physical treatment is totally biodegradable. For this type of wastewater, AOPs could be applied as a pre-treatment or post-treatment stage depending on the concentrations of the compounds.

A wastewater with high COD or TOC is usually treated in an anaerobic process for decreasing the organic load of the effluent. AOPs are useful to be employed as a post-treatment of anaerobically treated effluent to further destroy the residual compounds dissolved in the wastewater. For a wastewater with a high organic loading that is not highly biodegradable, it is useful to apply integrated processes such as anaerobic process, AOP, and another aerobic process in sequence. In the first stage (anaerobic process), a large portion of COD is removed from the effluent. Then in AOP, non-biodegradable residuals are decomposed to smaller and more biodegradable molecules which are suitable for aerobic treatment in the final stage. The effluents with high biodegradable organic loading could be treated by integrated anaerobic-aerobic-AOP processes. The first two stages are employed to reduce the COD, BOD, and TOC and further polishing. Using the last stage is also effective for post-treatment of residuals. Multi-stage integrated AOP-biological treatment is also advantageous for a class of wastewater solutions (bio-recalcitrant and inhibitory streams) for decreasing operating cost of the treatment but it requires a relatively higher capital cost. Instead of using multi-stage integrated AOP-biological systems, recycling is another alternative for higher removal rate of contaminants. Recycling is helpful to keep the fixed cost lower than that of multi-stage processes. The circulation ratio is an important factor to determine the efficiency of the integrated AOP-biological method. The optimization of circulation ratio is beneficial to maximize the system efficiency and minimize the operating cost.

## 5. BIODEGRADABILITY

In the integration of advanced oxidation technologies and biological processes, the main responsibility of advanced oxidation processes is to enhance the biodegradability of the wastewater not the complete oxidation, mineralization, and COD or TOC reduction because COD and TOC can be reduced during low cost biological method. Therefore, it is desirable to increase the biodegradability of wastewater in the AOP stage as much as possible. The biodegradability of a solution can be evaluated as follows:

- BOD enhancement

- BOD/COD enhancement

- BOD/TOC enhancement

Most of studies have emphasized on the enhancement of BOD/COD relative to the others. It is important to note that sometimes BOD/COD enhancement is due to only COD reduction and it may not result in a higher biodegradability. Although the COD of the solution is decreased, AOP may decompose the complex and toxic compounds and produce a relatively more toxic daughter compounds with lower BOD than that of the parent compounds. Therefore, the biodegradability is increased in the case of both COD or TOC reduction and BOD enhancement.

## 6. INTEGRATION OR COMBINATION?

In recent years, different studies have tried to increase the efficiency of AOPs by using various methods such as integrated (sequential) and combined (simultaneous) processes. As explained earlier, the main purpose of integrating different treatment methods is to enhance the process efficiency as well as to reduce the operating cost. On the other hand, a combined process is used for intensification of the process. Neelavannan et al. (2007) [27-28] showed that combined photocatalytic and electrochemical processes performed a better reaction blue dye degradation rate as compared to that of integrated processes. The main parameter in combined processes to evaluate the effectiveness of the system is the synergetic effect. Synergetic effect is a parameter that shows the enhancement of organic compounds' degradation under combined method relative to the linear combination (sequential) method. The synergetic effect could be estimated as follow [17]:

$$\text{Synergetic effect} = \frac{\text{Combined reaction rate constant}}{\text{Linear summation of individual methods rate constant}} \quad (1)$$

The existence of two or more advanced oxidation processes often results in a greater degradation rate due to several factors that are explained in details in the next sections. The design, construction, operation, and maintenance of combined (simultaneous) advanced oxidation processes is more difficult than those of the individual methods, but by combining various technologies, lower capital and operating costs are achievable. It is obvious that the purpose of combination of advanced oxidation processes is to enhance the degradation rate that is not achievable by a single process alone under the same condition. Several factors are required to be considered simultaneously in combined advanced oxidation technologies. These factors are as follows:

**Method:** The strength of different combined methods is useful to decide whether this hybrid system is beneficial. For those methods employed to degrade organic compounds or to enhance the biodegradability, the combined method which has the greatest removal rate would be the best choice. On the other hand, if the goal of the treatment is mineralization, it is better to select the combined system that has the highest TOC reduction rate.

**Residence time:** The product of the synergetic effect and residence time is equal to the summation of individual processes' residence times.

**Cost:** Fixed and operating costs of hybrid methods are less than those of the summation of different individual process. By increasing the synergetic effect, these costs can be even less. Synergetic effects of less than one are almost always not practical due to the lower degradation rate and higher maintenance cost. It is also not economical to combine different methods with the synergetic effect slightly greater than one when the contribution of a method is lower in the degradation of organic compounds and synergetic effect.

**Energy:** In combining different single processes, the amount of energy or power required for the degradation should be considered. Methods employing UV, ultrasonic irradiation, ozone generation, gas sparging, and mechanical mixing consume a higher amount of energy relative to others, but they enhance the degradation rate.

There are many studies in combining different AOPs such as combined photocatalysis and ultrasound [64-71], ozonation and ultrasound [72-74], photo-Fenton processes [75-77], and combined Fenton, photo-Fenton, and ultrasound [78-85]. Combining an advanced oxidation technology and biological process is very rare because hydroxyl radicals' formation during the AOPs may be inhibitory to biomass. Moreover, the presence of H<sub>2</sub>O<sub>2</sub> is also poisonous to microorganisms. Therefore, it is better to use the combined system in the AOP part to enhancing the oxidation and biodegradability in less time. In studying the behavior of the integration of combined AOPs and biological treatment processes, it is better to define a new parameter to depict the biodegradability enhancement due to the combination of different methods.

$$\text{Synergetic biodegradability enhancement} = \frac{\text{Biodegradability enhancement by combined process}}{\text{Total biodegradability enhancement by individual processes}} \quad (2)$$

This equation shows the amount of additional BOD produced by combined process. This equation is useful in evaluating the integrated AOP-biological process efficiency as the biodegradability enhancement is necessary to be achieved.

## 7. KINETICS AND MODELING OF INTEGRATED PROCESSES

AOPs have their own kinetics and mechanisms for oxidizing organic compounds depending on irradiation source characteristics and the type and the dose of reagents functioning in the reactor. Different studies carried out for modeling AOPs such as UV/H<sub>2</sub>O<sub>2</sub> [5, 86], photocatalysis [87], and Fenton [88-89]. A few studies were carried out for modeling of integration processes [86, 90-91].

### 7.1 BIOLOGICAL MODELING

Usually biological reactions are modeled by Monod [90, 92-95], Haldane [90], two-step Haldane [90], Contois [96-97], and Grau [98]. The Monod equation has been found as an acceptable and powerful mathematical expression fitted to experimental data described as follows [90]:

$$\mu = \mu_{\max} \frac{COD}{K_{COD} + COD} \quad (3)$$

where  $\mu$  and  $\mu_{\max}$  are the specific and maximum specific growth rates of microorganisms,  $K_{COD}$  is the half saturation constant, and COD is standing for any limiting organic source (COD concentration), respectively. In case of  $K_{COD} \ll COD$  that is applicable to no inhibition, Monod equation can be simplified as follows [90, 94]:

$$\mu = \frac{1}{V_{SS}} \frac{d(V_{SS})}{dt} = \mu_{\max} \frac{COD}{K_{COD} + COD} \cong \mu_{\max} \quad (4)$$

Cell yield coefficient can be defined based on the COD consumption and volatile suspended solids (VSS) production during aerobic biochemical degradation and it can be defined as follows [90]:

$$Y_{VSS/COD} = \frac{VSS - VSS_0}{COD_0 - COD} \quad (5)$$

where  $VSS_0$  and  $VSS$  are the initial and final volatile suspended solids in the bioreactor, and  $COD_0 - COD$  is the organic consumption during the biological treatment. Rivas et al., (2003) [91] also employed Equation (5) based on the utilization of biodegradable COD fraction.

Monod expression can be employed for modeling as follows:

$$-\frac{1}{[VSS]} \frac{d[COD]}{dt} = \frac{\mu}{Y_{VSS/COD}} = \frac{\mu_{\max} [COD]}{K_{COD} + [COD]} \cdot \left[ \frac{[COD]_0 - [COD]}{[VSS] - [VSS]_0} \right] \quad (6)$$

$$-\frac{d[COD]}{dt} = \frac{\mu_{\max} [VSS][COD]_0}{K_{COD}([VSS] - [VSS]_0)} - \frac{\mu_{\max} [VSS][COD]}{K_{COD}([VSS] - [VSS]_0)} \quad (7)$$

If  $A = \frac{\mu_{\max} [VSS][COD]_0}{K_{COD}([VSS] - [VSS]_0)}$ ,  $B = \frac{\mu_{\max} [VSS]}{K_{COD}([VSS] - [VSS]_0)}$ , and  $K_{COD} \ll [COD]$ , after integration of the equation, following equation can be achieved:

$$\ln\left(\frac{A + B[COD]}{A + B[COD]_0}\right) = Bt \quad (8)$$

A plot of the left hand side of Equation (8) versus t should give a straight line to find the parameters of interest.

## 7.2 MODELING OF ADVANCED OXIDATION TECHNOLOGIES

Modeling of the AOPs is carried out based on the summation of degradation rates in different methods such as direct photolysis, direct ultrasonolysis, direct ozonolysis, the degradation due to hydroxyl radicals attack, and the degradation due to the synergetic effect. A typical kinetics of US/UV/H<sub>2</sub>O<sub>2</sub> and US/UV reaction can be written based on the degradation rate of individual processes and the impact of the synergetic effect as follows [73, 83, 86]:

$$-\frac{dC_i}{dt} = K_{pyr}[C_i] + K_{OH}[C_i] + \phi_C I_0 \left( \frac{\epsilon_{C_i}}{\sum_i \epsilon_i C_i} \right) \left[ 1 - e^{-2.303L \sum_i \epsilon_i C_i} \right] - K_{synergy}[C_i] \quad (9)$$

where  $\phi_C$ ,  $I_0$ ,  $\epsilon_i$ , and  $C_i$  are quantum yield, light intensity, molar absorptivity, and the compounds' concentration.  $K_{pyr}$  and  $K_{OH}$  are the constant of pyrolytic decomposition rate of organic compounds and the constant of the rate of reaction between organics and hydroxyl radicals, respectively.  $K_{synergy}$  is the synergetic effect constant representing the degradation rate enhancement due to combined treatment methods. In the combined UV/US/H<sub>2</sub>O<sub>2</sub> processes, organic compounds are oxidized through direct photolysis, combustion or pyrolysis, free radical attack, and the synergetic effect predicted by combined system. If the completely mixed solution is assumed, the degradation of contaminants is due to the location of UV lamps, ultrasonic transducer, and the physical and geometrical characteristics of the reactor. The location of the ultraviolet lamps and ultrasonic irradiation is also very critical for determining the synergetic effect. The highest synergetic effect is predicted when the UV lamps bounded with ultrasonic irradiation field. In other words, maximum local volumetric rate of energy absorption (LVREA) and ultrasonic field overlap can produce a highest synergetic effect. Therefore, for designing an AOP system, the location of internal equipment employing for irradiation should be carefully selected to maximize the synergetic effect of the process.

The experiments for the advanced oxidation processes are usually conducted by optimizing the operating conditions and photoreactor characteristics since the efficiency of the AOPs is affected by various variables such as the concentration of initial compounds, residence time, H<sub>2</sub>O<sub>2</sub> dose, photocatalyst concentration, temperature, and pH. Therefore, it is necessary to employ the optimal condition. Recently, the experiments are conducted to analyze the effects of different parameters on the process effectiveness. Experimental design is also useful in order to avoid one-factor-at-a-time approach, where one variable was changed while keeping the others constant. Experimental design also helps to find the complex interaction between independent variables. Among these interactions, synergetic effect leads to the generation of higher hydroxyl radicals and it requires to be carefully optimized.

## 8. OPTIMIZATION OF THE INTEGRATED PROCESSES

Integrated processes are optimized to enhance the mineralization efficiency. Process optimization can be based on the residence time, the energy consumption, and the total cost. The optimization of each parameter depends on the environmental regulation, the process location, and characteristics of individual processes.

### 8.1 Residence time

The minimization of the total residence time of all processes involved in integrated system is the objective function of the optimization. The constraints are also the limits of residence times of individual processes including the mass balance of each component in every process. Therefore, the objective function of integrated processes based on the total residence time is as follows [12]:

$$\text{Minimize: } F = \theta_p + \theta_c + \theta_B \tag{10}$$

where  $\theta_p$ ,  $\theta_c$ , and  $\theta_B$  (h) are physical, chemical, and biological residence times, respectively. F (h) is the total residence time of the system. The constraints are usually defined such that  $\theta_p$  and  $\theta_b$  should be positive where  $\theta_c$  should be greater than a value so that a reasonable biodegradability is achieved.

### 8.2 Fixed cost

The fixed or capital cost of AOPs is relatively higher as compared to other treatment methods. Hirvonen et al. (1998) [99] provided the capital and operating cost of UV/H<sub>2</sub>O<sub>2</sub> (AOPs) and activated carbon. Estimated fixed costs of different treatment methods based on the depreciation period (40 years) are provided as follow [99]:

Photoreactors:

$$FC_C = \frac{85,000 + 40 \times 1,500}{(40 \times 24 \times 365) \left( \frac{V_C}{\theta_C} \right)} \times \left( \frac{1m^3}{1000L} \right) \tag{11}$$

where FCC (\$/L) is a typical UV/H<sub>2</sub>O<sub>2</sub> fixed cost, and V<sub>C</sub> (m<sup>3</sup>) is the volume of the photoreactor.  $\theta_c$  (h) is the residence time of the wastewater in the photoreactor. The fixed cost for a UV/H<sub>2</sub>O<sub>2</sub> process is usually \$58,000 plus the cost of UV lamp which is \$15,000 per year. The maximum allowable useful life estimate under U.S.A. income tax regulations is 40 years which can be considered as depreciation time.

Activated carbon:

$$FC_P = \frac{58,000}{(40 \times 24 \times 365) \left( \frac{V_P}{\theta_P} \right)} \times \left( \frac{1m^3}{1000L} \right) \tag{12}$$

where FCp (\$/L) represents the fixed cost of a typical activated carbon column and V<sub>p</sub> (m<sup>3</sup>) is the volume of the column. \$58,000 is the capital cost for a typical activated carbon column.

Biological reactor:

$$FC_B = \frac{(72 \times 40 \times 24 \times 365) \left( \frac{V_B}{\theta_B} \right) + 368,403}{(40 \times 24 \times 365) \left( \frac{V_B}{\theta_B} \right)} \tag{13}$$

where  $FC_B$  (\$/L) shows a typical activated sludge capital cost based on the bioreactor volume ( $V_B$ ) and the residence time ( $\theta_B$ ). \$368,403 is the capital cost for a typical biological treatment and \$72 is also required for the treatment of 1 m<sup>3</sup> wastewater.

### 8.3 Maintenance and operating costs

The operating cost of different processes is necessary to be optimized. The operating cost of AOPs is also high due to the continuous addition of reagents such as H<sub>2</sub>O<sub>2</sub> and Fe<sup>+2</sup>. Physical treatment methods utilizing an adsorbent are considered to be an additional expense for regeneration. Operating and maintenance cost of typical UV/H<sub>2</sub>O<sub>2</sub>, activated carbon, and biological processes are provided as follows [90, 99]:

$$OMC_C = \frac{2000}{\left(\frac{V_C}{\theta_C}\right)(24 \times 365)} \times \left(\frac{1m^3}{1000L}\right) \quad (14)$$

where  $OMC_C$  is the operating and maintenance costs for a typical UV/H<sub>2</sub>O<sub>2</sub> system and \$2,000 is the operating cost estimated for 40 years.

$$OMC_P = \frac{1,200 + 0.29V_P}{\left(\frac{V_P}{\theta_P}\right)(24 \times 365)} \times \left(\frac{1m^3}{1000L}\right) \quad (15)$$

where  $OMC_P$  is the maintenance and operating cost of a typical activated carbon column. \$1,200 is the operating and maintenance cost estimated for 40 years, and 0.29 [\$m<sup>3</sup>] is the cost for the regeneration and reactivation of the carbon bed.

$$OMC_B = \frac{4.58 \times (24 \times 365) \left(\frac{V_B}{\theta_B}\right) + 36,295}{\left(\frac{V_B}{\theta_B}\right)(24 \times 365)} \times \left(\frac{1m^3}{1000L}\right) \quad (16)$$

where  $OMC_B$  is the maintenance and operating cost of a typical biological treatment. \$36, 295 is the operating and maintenance cost predicted for 40 years plus the 4.58 [\$m<sup>3</sup>].

Above Equations (10-16) are useful for optimizing the cost of various integrated processes containing advanced oxidation technologies.

## 9. CONCLUDING REMARKS

To achieve a cleaner water and healthier environment, more effective and powerful treatment methods are required. The integration of such methods is useful in order to fulfill the environmental regulations. Integration of physical, chemical, and biological treatment processes are useful to take advantages of the methods and to minimize the drawback of each methods. Anaerobic degradation is very helpful for treating high organic loading wastewater with lower energy consumption. Aerobic methods are usually employed to polish residuals. Therefore, in some cases, more than one biological method is required for a better treatment. Intensification of AOPs is one of the challenges of researchers in this area. Authors are trying to develop more effective and economical ones. Combining different reagents and irradiation sources are used to achieve higher synergetic effects for biodegradability enhancement. Modeling and optimization of integrated systems are also valuable to be extended to similar cases that might be practical for scale up. The effect of different parameters such as residence time, temperature, pH, the presence of different ions and acids, reagents doses, irradiation sources, recycling ratio is better to be embedded in the model. An optimization determines the optimal residence time, optimal size of the

equipment, optimal reagents doses, optimal operating condition such as oxygen concentration in the bioreactor, and optimal biodegradability achieved after advanced oxidation process.

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