



Review Article

Advanced Oxidation Processes for Textile Wastewater Treatment

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Abstract: Advanced oxidation is one of the potential alternatives to decolorize and to reduce recalcitrant wastewater loads from textile dyeing and finishing effluents. This process implies generation and subsequent reaction of hydroxyl radicals, which are the most powerful oxidizing species after fluorine. Among AOPs, treatment with ozone (often combined with H_2O_2 , UV, or both), an UV/ H_2O_2 system, or Fenton and Photo-Fenton type processes have proven to yield very good results either for complete mineralization of reactive dyes or for their transformation into less complex structures that are more easily biodegradable. Particularly, we summarize recent researches in the AOP treatment using O_3 alone and or in combination with UV, US and H_2O_2 of textile wastewater for complete color and COD removal and decrease the toxicity of the treated wastewater for water.

Keywords: Advanced Oxidation Processes, Ozone, Ultraviolet, Color Removal, Wastewater, Textile Industry

1. Introduction

The goal of any AOPs design is to generate and use hydroxyl free radical ($\cdot OH$) as strong oxidant to destroy compound that cannot be oxidized by conventional oxidizing agent. In Table 1, some oxidation potentials of several chemical oxidizers are given. Advanced oxidation processes are characterized by production of $\cdot OH$ radicals and selectivity of attack which is a useful attribute for an oxidant [1-5].

Table 1. Oxidizing potential for conventional oxidizing agents.

Oxidizing agent	Electrochemical oxidation potential (EOP, V)	EOP relative to Chlorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

Hydroxyl radicals are extraordinarily reactive species; they attack the most part of organic molecules easily and also characterized by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOPs is also enhanced due to their different possible ways for hydroxyl radical production, allowing a better compliance with specific treatment requirements [6-9].

There are four well-known methods for generating hydroxyl radicals without using light energy. Three of the methods involve the reaction of ozone while the fourth uses the Fe^{+2} ions.

O_3 / OH^-

O_3 / H_2O_2

$O_3 / \text{Catalyst}$

Fenton's Reaction (Fe^{+2} / H_2O_2)

There are many different UV light enhanced treatment processes available. The following are the five most common.

$O_3 / UV-C$

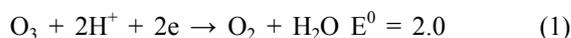
$H_2O_2 / UV-C$

O₃ / H₂O₂ / UV-C
 Photocatalytic (TiO₂ / UV-A)
 Photo Fenton (Fe⁺² / H₂O₂ / UV-A)

2. Treatment of Textile Wastewaters with Ozone

Chemical oxidation with ozone is one of the most suitable chemical oxidation processes for effective color removal from textile effluents, with simultaneous interaction and breakdown of refractory organic matter resistant to biodegradation, without leading to sludge production [10]. Concerning COD removal, ozone is considerably less efficient [11-14]. However, the ozonation has proven to be rather inefficient for the reduction in COD, whereas, its application in one step for color removal and partial oxidation to improve biodegradability seems to be more promising [15]. It is stated that an increase in the ratio of BOD/COD after ozonation results from an improved biodegradability of toxic substances.

It is well known that ozone is a strong oxidant $E^0 = 2.08$ V (Eq. 1), and able to form the more powerful, nonselective oxidant of the hydroxyl radical ($E^0 = 2.80$ V) at high pH values. Due to this high oxidation potential, ozone can effectively break down the complex aromatic rings of dyestuffs, resulting in the decolorization and transformation of the dye compounds. Actually, ozone can react with reactive dyes more effectively than with other types, such as disperse, acid and sulfur dyes [16].



Because ozone is an unstable molecule, it should be generated at the point of application for use in treatment purposes. It is generally formed by combining an oxygen atom with an oxygen molecule (Eq. 2). The reaction is endothermic and requires a considerable input of energy.

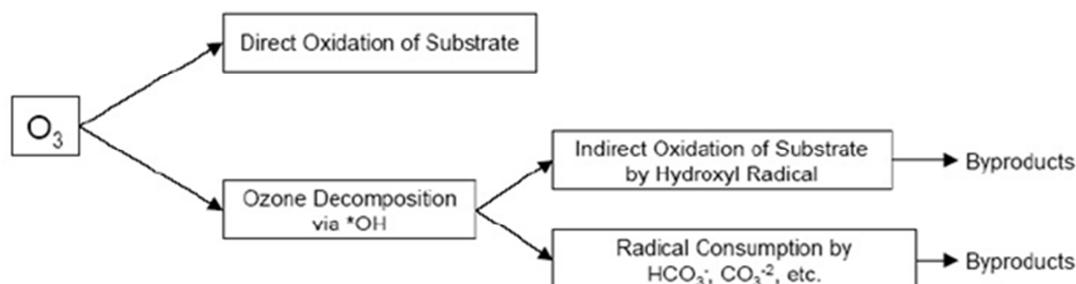


Figure 1. Oxidation reactions of compounds during ozonation.

The two oxidation pathways compete for substrate (compounds to oxidize). The direct oxidation with aqueous ozone is relatively slow (compared to hydroxyl free radical oxidation) but the concentration of aqueous ozone is relatively high. On the other hand, the hydroxyl radical reaction is fast, but the concentration of hydroxyl radicals under normal

Ozone can be produced by several ways, although one method, corona discharge, predominates in the ozone generation industry [17, 12-14]. Corona discharge, also known as silent electrical discharge, consists of passing an oxygen-containing gas through two electrodes separated by a dielectric and a discharge gap. Voltage is applied to the electrodes, causing an electron flow through across the discharge gap. These electrons provide the energy to disassociate the oxygen molecules, leading to the formation of ozone [18].

Ozone alone and in combination with UV light, catalyst, ultrasound or activated carbon has been successfully applied to textile industrial effluents. The advantage is that ozone can be applied directly in its gaseous state and therefore doesn't increase the volume of wastewater and sludge. Typically, ozonation doesn't yield complete mineralization to CO₂ and H₂O but leads to formation of partial oxidation products such as organic acids, aldehydes and ketones [19, 3-5].

Although some treatment processes (adsorption, coagulation etc.) achieve reduction in COD, substantial amounts of residual color remain. Several different methods have been developed for treatment of textile effluents. The ozone method is known to be effective for decomposing organic chemicals containing carbon-carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics, heterocyclics, carbon-nitrogen double bonds, carbon hydrogen bonds, silicon-hydrogen and carbon-metal bonds. Most of the dyestuffs are composed of aromatic organic compounds, so the ozone method is getting more attention with the prediction that it could decompose various kinds of dyestuffs. It is reported that ozone is an effective agent for reducing the color of dyestuff wastewater [20, 12-14].

As shown in Figure 1, ozone can react by either or both modes in aqueous solutions: direct oxidation of compounds by molecular ozone (O₃), or indirect oxidation of compounds by hydroxyl free radicals produced during the decomposition of ozone [21].

ozonation conditions is relatively small [21]. Hoigné and Bader (1976) [22], found that under acidic conditions, the direct oxidation with molecular ozone is of primary importance; and, under conditions favoring hydroxyl free radical production, such as high pH, exposure to UV, or

addition of hydrogen peroxide, the hydroxyl oxidation starts to dominate.

In fact, elimination of color from textile wastewater is of both immediate and long term interest to textile manufactures, because either currently or in the future it is necessary to limit the discharge of color from textile manufacturing plants. Furthermore, elimination of color from dye bath water after dyeing may make the water suitable for reuse in the dyeing process or in some other process in the manufacturing plant.

3. Ozonation at High pH

The rate of disintegration of ozone in water rises as pH increases. For example, at pH 10, the half-life of ozone in water becomes less than one minute. As a result of the combination of reactions with molecular ozone and reactions with $\cdot\text{OH}$ radicals, oxidation of pure species can take place. The reaction involving hydroxide ions and ozone leads to the creation of the super-oxide anion radical O_2^- and hydroperoxyl radical HO_2 . The reaction involving ozone and the super-oxide anion radical creates the ozonide anion radical O_3^- . The radical instantly decays releasing $\cdot\text{OH}$ radical. Three ozone molecules generate two $\cdot\text{OH}$ radicals (Eq. 3) [23, 12-14].



4. Photochemical Oxidation Processes

4.1. Mechanism of Photo Oxidation

Advanced oxidation processes have gained attention due to their efficiency and ability to treat almost all solid components in textile effluents. Photo oxidation can take place at any temperature and pressure and does not produce any secondary components) [24].

The basic mechanism of advanced oxidation processes is the production of $\cdot\text{OH}$ ions [1, 25-26]. These are strong oxidants capable of destroying components that are hard to be oxidized. Generation of $\cdot\text{OH}$ radicals are generally accelerated by the combinations of some commonly used oxidants such as H_2O_2 , UV, O_3 , TiO_2 , Fe^{2+} , electron beam irradiation and ultra sound [1, 12-14, 26].

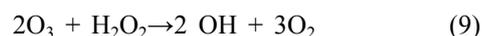
$\cdot\text{OH}$ radicals are considered as reactive electrophiles due to their preference to electrons and hence they react rapidly towards electron rich organic compounds [27]. The radicals are found to have an oxidation potential of 2.80 V and are hence found to oxidize substances more quickly than conventional oxidants [27-28]. The organic substances are first attacked by the generated hydroxyl radicals (Eq. 4), followed by hydrogen abstraction (Eq. 5) and then the electron transfer (Eq. 6) [27].



Where: R is reacting organic compound.

4.2. Ozone/UV (O_3/UV) Process

Photolysis of ozone in water with UV radiation in the range of 200-280 nm can lead to yield of hydrogen peroxide. Hydroxyl radicals can be generated by this produced hydrogen peroxide under UV radiation and/or ozone as given equations below:



Starting from low pressure mercury vapour lamps, all kinds of UV light sources can be used for this process. Because, O_3/UV process doesn't have the same limitations of $\text{H}_2\text{O}_2/\text{UV}$ process, low pressure mercury vapor UV lamps are the most common sources of UV irradiation used for this process. Many variables such as pH, temperature, scavengers in the influent, turbidity, UV intensity, lamp spectral characteristics and pollutant type(s) affect the efficiency of the system [12-14, 18, 29]. Number of laboratory, pilot and full scale applications of Ozone/UV and Hydrogen peroxide/UV processes can be found in literature.

5. Literature Review of the Advanced Oxidation Processes (AOPs)

Many investigations have shown that ozonation was highly effective in breaking down the straight, unsaturated bonds in the dye molecules, causing rapid decoloration of textile wastewater. The capability of ozone in oxidizing various pollutants by direct attack on different bonds, ($\text{C}=\text{C}$) bond and aromatic rings, are further enhanced in the presence of hydrogen peroxide and or UV due to the generation of highly reactive $\cdot\text{OH}$ radicals. The dissociation of hydrogen peroxide results in the formation of hydroperoxide ion, which attacks the ozone molecule resulting in the formation of hydroxyl radicals [3-5, 28].

Ozonation produces compounds that may elicit toxicity or mutagenicity, but most researchers found less toxicity in ozonated wastewater samples and considerable biodegradability improvement particularly in the case of textile dyes. It is important to optimize the applied ozone dose and ozonation time to achieve a maximum biodegradability of the specific pollutant that might diminish with extended ozone exposure and higher COD reduction [30-31].

Sarikaya and Sevimli (2002) and Konsowa (2003) [32-33], stated that color removal using ozonation from textile wastewater is depended on initial dye concentration and also initial COD. In parallel; Gianluca and Nicola (2001) stated that COD removal from a textile wastewater, which has been pre-treated, was depended on the initial COD of the wastewater. In their study, 67% and 39% COD removal were realized when the initial COD was 160 and 203 mg/L, respectively.

Koch *et al.* (2002) [34], achieved 50% COD removal after 60 min. with 18.5 mg/L ozone concentration and 40% COD removal after 90 min with an ozone concentration of 9.1 mg/L. Ciardelli *et al.* (2001) [11], conducted a study on pre-treated wastewater coming from a fulling and dyeing plant used to dye fabrics, hanks, skeins, tops and flocks of different natural and synthetic fibres and mixture of both. They achieved 67% COD removal and 99% color removal in the effluents with 40 g/m³ ozone concentration when initial COD concentration was 160 mg/L and stated that higher doses do not give further benefits in terms of water discoloration.

In a similar way, Doğruel *et al.* (2002) [10], tested ozonation efficiency both in terms of ozone flow-rate and contact time; a level of around 60 mg/min was determined as the optimum ozone flow-rate, providing almost complete color removal. Total COD reduction, however, could not be improved beyond 32%, even for extended contact times.

Several researchers have reported high color removal efficiencies by ozonation for different dye types. For example, Kabdaşlı *et al.* (2002) [35], realized 99% color removal with 63 mg/min ozone dose within 45 minutes on reactive dyes (Procion). Sundrarajan *et al.* (2007) [19], achieved complete color removal after ozonation for 40 min at an ozone consumption of 76.5 mg/L. However, COD removal efficiency (22%) was not as high as color removal efficiency in the study. In the research of Solmaz *et al.* (2006) [36], ozonation resulted in 97% color removal and 43% COD removal, with 20 mg/min ozone dose.

On the other hand, some researchers stated that ozone can decolorize all dyes, except non-soluble disperse and vat dyes whose reactions with ozone are slower and take longer time [37-38]. However, in general case, treatment with ozone on textile wastewaters gives satisfactory results on color removal, while for COD; removal efficiencies are not so satisfactory. The low COD reduction is attributable to the fact that the structured polymer dye molecules are oxidized by ozonation to small molecules, such as acetic acids, aldehyde, ketones, etc., instead of CO₂ and water. These small molecules still possess a considerable amount of COD [39].

Roushdy (2007) [40], concluded that, the ozonation process is a very effective process for the decolorization of textile wastewater, as we can reach 98% decolorization in few minutes. Adjusting some controlling factors will give high result of decolorization. It was recommended that, there is a direct need to enhance the ozonation process as a very effective method for wastewater treatment to modify the allowable limits for discharging wastewaters to the marine environment.

Chen (2009) [41], investigated the feasibility of applying ozone to reduce the color content of wastewater caused by two commercial reactive dyes (Blue-19 and Orange-13). Results showed that some experimental variables such as ozone dosage and pH dominated the effectiveness of the decolorization process. The color content could be reduced from 2000 to 200 ADMI (American Dye Manufacture Institute) during reaction time of 30 min with the ozone input rate of 2.66 g/h. The pH values of 3 and 10 favored

decolorization of Blue-19 and Orange-13, respectively. This was attributed to the predominance of reactive and oxidizing species of molecular ozone and hydroxyl radicals at low and high pH. Moreover, molecular ozone was more selective to certain dye structures during the oxidation process. Kinetic analyses showed that decolorization of Orange-13 and Blue-19 followed first-order kinetics. The degree of decolorization was primarily proportional to the ozone dosage.

Khadhraoui *et al.* (2009) [42], investigated the degradation and mineralization of an azo-dye, the Congo red, in aqueous solutions using ozone. Through this work the phytotoxicity and the inhibitory effects on the microbial activity of the raw and the ozonated solutions with the aim of water reuse and environment protection was also studied. Decolorization of the aqueous solutions, disappearance of the parent compound, chemical oxygen demand (COD) and total organic carbon (TOC) removal were the main parameters monitored in this study. To control the mineralization of the Congo red, pH of the ozonated solution and heteroatoms released from the mother molecule such NH₄⁺, NO₃⁻ and SO₄⁻² were determined. It was concluded that ozone by itself is strong enough to decolorize these aqueous solutions in the early stage of the oxidation process. Nonetheless, efficient mineralization had not been achieved. Significant drop in COD (54%) was also registered. The extent of TOC removal was about 32%. Sulfur heteroatom was totally oxidized to SO₄⁻² ions while the central -N-N-azo ring was partially converted to NH₄⁺ and NO₃⁻. Results of the kinetic studies showed that ozonation of the selected molecule were a pseudo-first-order reaction with respect to dye concentration. The obtained results also demonstrate that ozone process reduced the phytotoxicity of the raw solution and enhanced the biodegradability of the treated azo-dyes-wastewater. Hence, this show that ozone remains one of the effective technologies for the discoloration and the detoxification of organic dyes in wastewater.

Alessandra *et al.* (2009) [43], investigated ozonation of two azo dyes in a monitored bench scale bubble column reactor (8.5 L), varying liquid media salt content (0, 1, 40 and 100 g/L, NaCl). In the experiment with Orange II, pH varied (5, 7.5 and 9) but ozonation of Acid Red 27 was performed at pH 7.5. Ozone self-decomposition rate-constant increased with salt concentration. Color removal was very effective and fast achieved under all experimental conditions. For the two azo dyes tested, more than 98% of color intensity was removed in 30-min ozonation assays. However, only partial mineralization of azo dyes (45% Orange II; 20% Acid Red 27) was attained in such experiments. The degree of mineralization (TOC removal) was negatively affected by salt concentration. Biodegradation assays conducted by respirometry revealed the inhibitory effect of dye degradation products formed during ozonation. Ozonation was very effective to decolorize solutions of Acid Red 27 and Orange II, even at the higher salt concentration (100 g/L), the color was removed at with higher effectiveness more than 98%, after 30 min of ozonation. Ozonation products had a significant

inhibitory effect on the activity of the microorganisms employed in the respirometric assays. This was particularly demonstrated by the results obtained in assays conducted with a readily biodegradable substrate added to the ozonated samples.

Somensi et al. (2010) [44], studied the ozonation of raw textile wastewater that conducted in a pilot-scale plant. The efficiency of this treatment was evaluated based on some parameters such as color removal and soluble organic matter which measured as chemical oxygen demand (COD), at two pH values (9.1 and 3.0). Identification of intermediate and final degradation products of ozone pre-treatment, as well as the evaluation of the final ecotoxicity of pre-treated wastewater (Lumistox test), was also carried out. After 4 h of ozone treatment with wastewater recirculation (flow rate of 0.45 m³/h) the average efficiencies for color removal were 67.5% (pH 9.1) and 40.6% (pH 3.0), while COD reduction was 25.5% (pH 9.1) and 18.7% (pH 3.0) for an ozone production capacity of 20 g/h.

Furthermore, ozonation enhances the biodegradability of textile wastewater (BOD₅/COD ratios) by a factor of up to 6.8-fold. A GC-MS analysis of pre-treated textile wastewater showed that some products were present at the end of the pre-treatment time. In conclusion, pre-ozonation of textile wastewater is an important step in terms of improving wastewater biodegradability, as well as reducing acute ecotoxicity, which should be removed completely through sequential biological treatment.

Palit (2010) [45], studied a massive and considerable amount of effluent generated in a textile industry and allied industries. Dyes used in the dyeing section of a textile industry are a constant, intense and persistent source of concern to the environmental engineer and to the common mass in general. This dye effluent/waste cannot be degraded with the help of primary and secondary treatments. Primary treatment involves coagulation and flocculation while secondary treatment encompasses activated sludge process. The study reported the importance, urgency and aim of a tertiary treatment process such as ozone-oxidation or ozonation. It was also mentioned that the understanding of the dependence of order of reaction on pH of the solution and oxidation-reduction potential. The ozonation of dye was done in a bubble column reactor-fixed bed and without media.

Tehrani and Amini (2010) [46], compared the treatment efficiency of O₃ and O₃ assisted UV processes for the oxidation of simulated dye bath effluent containing a mixture of a reactive dye (C.I. Reactive Blue 19) and various dye auxiliary chemicals. The color, COD and TOC removal rates were assessed for different processes. The effect of initial dye concentration and presence of sodium hydroxide and sodium carbonate on decolorization kinetics were studied. It was noted that the decolorization kinetics decreased by increasing of initial dye concentration and addition of sodium hydroxide. Moreover, the addition of sodium carbonate resulted in a lower COD removal. The experimental results showed that ozonation combined UV irradiation (9-watt low-pressure mercury lamp) was slightly more efficient than ozonation

alone in COD removal with no change in color removal efficiencies. At an initial pH of 6.2, bulk temperature of 25 °C, ozone dosage of 55 g/m and initial dye concentration of 800 mg/L, the TOC removal efficiency of RB19 reached 19% and 27% after 90 min for O₃ and O₃ assisted UV, respectively.

Pang et al. (2011) [47], studied the technologies to be applied in conjunction with sonochemical degradation process for enhancing degradation of recalcitrant organic compounds. The addition of catalysts and chemical additives with ultrasonic irradiation are particularly reviewed as effective methods to increase the generation of free [•]OH. In this study, combination of ultrasound and different chemical additives such as ozone and H₂O₂ and fenton reagent were tested.

Abidin et al. (2011) [48], evaluated the characteristic of COD and colour removal of azo dye by Advanced Oxidation Process (AOP) and biological treatment for applying in azo dye industrial effluent treatment. They selected Reactive Red 120 dye among other azo dyes due to its high solubility in aquatic environment. It was noticed that AOP could improve colour removal of reactive red 120 in comparison to ozonation, due to acceleration of ozone decomposition by hydrogen peroxide and eventually enhanced the production of the hydroxyl radical, which is quickly oxidize colour impacting functional group in reactive red 120. The optimum COD removal by AOP was achieved at 1 mg H₂O₂/mg O₃. Further addition of hydrogen peroxide could increase COD, which probably due to residual H₂O₂ that is not completely react with ozone to produce radical. In the multi-stage ozonation biological treatment, the role of ozonation seemed to breakdown the azo dye molecule and created ozonation product that is easily biodegraded in biological treatment. On the other hand, advanced oxidation process tends to decompose ozone and hydrogen peroxide to produce [•]OH radical, and react with azo dye through radical mechanism to completely mineralized azo dye.

Eren (2012) [49], summarized the use of ultrasound with biochemical, electro-chemical, ozonation, photolysis, photocatalysis and fenton processes for the degradation of mostly textile dyes and dye bath. There are few studies about ultrasonic degradation of textile effluents or wastewater due to highly variable contents. It was found that the most common use of ultrasonic irradiation for dye degradation is the combination with the heterogeneous catalysts/adsorbents. Fenton reaction is already fast itself and gives effective degradation during the oxidation. Therefore, addition of ultrasonic irradiation to Fenton oxidation was less effective compared to other auxiliary processes. It was noted that ultrasonic irradiation had a negative effect on dye degradation during combination with electro oxidation process.

Parsa and Negahdar (2012) [50], investigated the degradation of Acid Blue 92 (AB92) by ozonation, O₃/H₂O₂ and O₃/Activated carbon (AC). It was observed that in ozonation and O₃/H₂O₂ processes with gained pH and in O₃/AC with reducing pH to 4, AB92 has relatively a better degradation rate. However, there had been a higher removal rate by increasing H₂O₂ concentration and reducing initial dye concentration. Effect of experimental parameters such as pH,

H₂O₂ concentration, initial dye concentration, activated carbon dosage and salt existence such as sodium chloride, sodium sulfate, sodium carbonate and sodium bicarbonate on the reaction was also studied. The criterion for progress of organic pollutant removal and mineralizing was alterations in chemical oxygen demand (COD) levels which were measured several times using Open Reflux method. The results indicated that the removal of COD in ozonation, O₃/H₂O₂ and O₃/AC processes were 30%, 80% and 100% respectively. However, addition of electrolyte caused a decrease in degradation rates.

Mitrovic *et al.* (2012) [51], studied the photochemical decolorization of C.I. Reactive Orange 16 (RO16) azo dye, by the UV/H₂O₂ process using a batch photoreactor with UV lamps emitting at 254 nm. Complete decolorization of 50 mg/dm³ initial dye concentration was achieved in less than 6 min under optimal conditions (25 mM initial peroxide concentration, pH 7.0 and 1950 uWcm⁻² UV light intensity). The effects of experimental variables, such as initial pH, initial concentration of H₂O₂, initial dye concentration, and the intensity of UV light were studied. The highest decolorization rates were realized at a peroxide concentration ranged from 20 to 40 mM, above which decolorization was inhibited by the scavenging effect of the peroxide. The decolorization was more efficient in neutral pH values. The efficiency of the process was improved with lower initial dye concentrations and at higher intensities of UV.

Arlindo *et al.* (2013) [52], observed that different dyes can exhibit markedly different reaction rates with ozone. These observations can raise the concern that in a mixture of dyes one of them can be over-oxidized while the other remains under oxidized (i.e. exhibiting colour). The study concluded that, the effect of pH on decolorization also deserves additional investigation; moreover, the influence of pH on the oxidation rate of the mono azo dye Acid Orange 7 (AO7), which considered one of the most difficult dyes to degrade, was studied in a homogeneous medium. The results have revealed an increase of nearly two orders of magnitude in the AO7 decolorisation rate when pH increased from 3 to 8.2. This effect was only slightly diminished when the radical scavenger was added. Competitive studies were performed between AO7 and the anthraquinone dye Acid Green 27 (AG27), which exhibits a much faster reaction rate. Furthermore, when the two dyes were mixed together, the AO7 decolorisation rate increased markedly, approaching the AG27 values, even under conditions that favour the undissociated species (pH = 2.7). This can be a very positive practical result as the charged ozone can be consumed almost indistinctly by the two dyes.

Bharadwaj and Anil (2013) [53], studied the treatment of synthetic dye solution of Acid Red 131 dye in a batch reactor using ozonation where ozone was produced in ozone generator by corona discharge. The amount of ozone consumed in the reaction was determined by measuring the ozone concentration at the inlet and outlet of the reactor using ozone analyzer. The effect of ozone dose, initial dye concentration and solution pH on the rate of decolorization

was studied and the results were analyzed in terms of colour removal efficiency. They noticed that the colour removal efficiency was found to increase with increasing of ozone dose and decrease with increasing in initial dye concentration of the synthetic dye solution. The results with Acid Red 131 synthetic dye solution showed that maximum decolorization was obtained at the solution pH 11. A 100% colour removal was obtained after 12 min of ozone treatment. Dye concentration, ozone concentration and pH of the solution were found to have a considerable effect on decolorization of the Acid Red 131 dye.

Zhou *et al.* (2013) [54], proved the promotion effects of ultrasonic on malachite green (MG) decolorization in the ultrasonic-assisted ozone oxidation process (UAOOP), and they also proposed the possible pathway of MG degradation. When ultrasonic (US) was applied with ozone simultaneously, the apparent pseudo-first-order rate constant (K_{app}) increased, and the time of MG decolorized to the half of initial concentration (T_{1/2}) shortened 185s (1000 mg/L). Moreover, the stoichiometric ratio (Z_{app}) between O₃ and MG was enhanced by US to 2.0 mol, saving 11% of oxidant addition, comparing to the individual ozone process. These results indicated that the application of US can reduce reaction time and dose of ozone addition, also, these result suggested that the reaction between MG and hydroxyl radical was substitution reaction rather than adduct reaction.

Mehmood *et al.* (2013) [55], harnessed the reuse potential of sewage wastewater (SWW) using integrated wastewater treatment irradiation, H₂O₂ oxidation and sand filtration separately. Composite sample of SWW was collected from inlet of sewage wastewater treatment plant. The SWW sample was batch wise subjected to activated sludge process (ASP), ozonation, UV irradiation, H₂O₂ oxidation and sand filtration separately for different time intervals (i.e. 0 to 60 min) and concentrations of H₂O₂ (0.1 to 1.0 ml/L), followed by the integration of all processes at their optimum conditions. Color reduction was much higher and faster than COD in all tested treatment processes. Ozonation was the fastest process to remove 78% color in 30 minutes, however; ASP was more economical for the same efficiency but requires high hydraulic retention time (HRT). Increase in UV irradiation time reduced COD and color by 54 and 69% after 60 min, respectively. Integration of 4 h ASP, 24 min ozonation and 10 min UV exposure with 1 ml/L H₂O₂ yielded 98 and 100% COD and color reduction, respectively.

Hassaan *et al.* (2016a) [12], investigated the efficiency of detoxification and decolorization of Direct Blue 86 dye solution in fresh and sea water using ozone and ozone/UV treatment processes. Regarding the results obtained, the ozone treatment proved to be highly effective for complete color removal but had provided more than 62% reduction of COD. The oxidation of the DB-86 dye followed first-order kinetics in respect to initial dye concentration. Color removal efficiency was higher in case of ozone alone when compared to O₃/UV combination, which may be explained as a result of the increase in the solution's temperature during O₃/UV process. That had an important influence on the half-life time

of ozone. Furthermore, GC/MS used for identifying the ozonation by-products as well as evaluating the degradation of the treated aqueous solution showed no toxic compounds since the GC/MS. diagram showed no peaks for toxic compounds such as phenols or aromatic amines, which are expected to have from dyes degradation. The obtained results from the toxicity test on Rotifer *B. plicatilis* also revealed that the ozonation processes reduced the zooplankton toxicity of the raw solution.

Hassaan et al. (2016b) [13], study the efficiency of using ozone and ozone combined with UV for color removal and detoxification of an aqueous solution of Mordant Violet 40 dye. The major conclusions derived from the work are as follows: ozone treatment proved to be very effective for complete color removal but provided only partial reduction of COD which is in agreement with many reported work as mentioned above in the results and discussion section. The oxidation of the MV-40 dye in freshwater followed the second-order kinetics and color removal efficiency was higher in case of UV and O₃ combination compared to ozone alone and it attributed to the production of more hydroxyl radicals, which were more efficient for mineralization. The application of the same methods for the treatment of MV-40 dye solution in seawater was studied and gave mainly similar results obtained for fresh water. Furthermore, GC-MS analysis for identifying the ozonation by-products as well as evaluating the degradation of the treated aqueous solutions, showed no toxic compounds. The obtained results also revealed that advanced oxidation processes reduced the zooplankton toxicity of the raw solution.

Hassaan et al. (2016c) [14], examined the possibility of applying ozone (O₃) and O₃ combined with ultraviolet (UV) to degrade the content of seawater containing Direct Yellow 50 dye. The Experimental parameters such as initial dye concentration and time of reaction were assessed in a batch reactor to achieve the optimum operating circumstances. The Results of this study showed that more than 88% color removal was obtained after 35 min of O₃ treatment (for 100 ppm dye concentration) and also partially removal of COD. These results also indicated that the application of O₃ is more effective than UV assisted Ozonation to reduce the reaction time. Also, Gas Chromatography Mass Spectrum analysis of treated synthetic dye solution was performed at the end of the pre-treatment time to the final degradation products of Direct Yellow 50 dye and showed no toxic compounds.

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