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Current Trends on the Utilization of Ozonation Treatment Process for the Remediation of Dye Wastewater: A Short Review

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Remediation of dye wastewater is necessary to prevent further pollution of the world's waterways. Dye effluents pose a threat not only to human health but also to aquatic life. Various chemical processes have been used to address this issue, and advanced oxidative processes (AOPs) have shown tremendous promise in recent years. Ozonation has been used to successfully treat and decolourise various types of wastewaters including dye wastewater. This process requires few prerequisite chemicals, minimises sludge generation and consolidates the removal of both colour and organic matter into a single step. This review aims to discuss current trends in the utilisation of ozonation treatment for the remediation of dye wastewater, as well as economic aspects and cost efficiency in the hope of eliciting further interest in potential new avenues within this field.

Key words: Dye, wastewater; advanced oxidative process, ozonation; hybrid ozonation process

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Water is regarded as one of the most important primary resources available on Earth. It is found everywhere: on land, in the oceans, in the atmosphere, and even within every living creature. The adult human body is approximately 70-75% water in terms of fat-free mass [1]. Without water, living organisms cannot survive on Earth. Good water quality is important for the well-being of all living creatures. In the recent COVID-19 pandemic, the importance of water was once again highlighted, due to the need for good hygiene practices. According to Cook and Makin, household water use increased 15-20 %, while businesses saw a decline of 30-50 %. Therefore, public health relies on the availability of clean and usable water [2].

Water scarcity caused by environmental pollution is an inevitable consequence of rapid industrialization and human activities. Dye wastewater, a major sources of water contamination, has caused serious environmental degradation and poses a serious threat to water bodies as well as to human health [3]. Dyes are used in various industries such as cosmetics, textiles, food and beverage, paper, leather, printing, pharmaceuticals, ceramics, and paints [4,5]. Dye-containing wastewater has a significant impact on the pH, BOD and COD of the water source it is being released into [6]. Out of the various types of dyes available, azo dyes are among the most popular, comprising about 65-70 % of the total dyes produced [4].

The presence of dyes in water reduces the dissolved oxygen (DO) level, blocking sunlight from entering the water system and obstructing photochemical reactions [7]. Most dyes have been found to be toxic and carcinogenic. The release of dyes into the aquatic ecosystem poses a threat to both humankind and aquatic life [8]. Dyes are visible at a concentration as low as 1 mg/L [9], and this negatively affects the clarity and aesthetic quality of water. Therefore, dye-containing wastewater needs to be treated before being discharged. Many physical, chemical, and biological methods of treating wastewater have been tested to various degrees of success. Physical methods for dye removal such as coagulation or flocculation have the disadvantage of sludge formation, whereas the filtration method requires high maintenance costs [10]. Chemical methods merely transform the pollutants from one phase to another, which causes undesirable secondary pollution [11,12]. Biodegradation methods are unsuitable to treat dye-containing wastewater due to its low BOD_5/COD ratio, which is an indicator of low biodegradability [13]. Furthermore, dyes generally have high structural stability, complex molecular structures and are toxic to microbes, which limits the biodegradation process [8,11]. The functional groups in dyes such as carboxylic, amine and azo groups make dye wastewater difficult to treat with conventional methods [14].

Aside from conventional treatment processes, ozonation is an advanced oxidation process (AOP) which generates highly reactive oxidative species (ROS) and has been proven to be an efficient method for the treatment of dye-containing wastewater [15–21]. This review explores current trends in the utilization of the ozonation treatment process for the remediation of dye wastewater. The challenges of ozonation and future perspectives are also presented.

1. Dyes

A dye is a colorant that is used to impart colour to a material or product in order to make the product more attractive and create a sensation in terms of mood and appearance [22]. Natural dyes are obtained from natural (vegetable, animal or mineral) sources whereas synthetic dyes are derived from organic or inorganic compounds [22,23]. Natural dyes are not harmful to the environment as they are derived from natural resources. However, synthetic dyes, which have received much attention due to their wide range of colours, low cost and ease of synthesis, are highly toxic [3]. The earliest use of dyes was found in cave paintings, and can be traced back to approximately 30,000 years ago [24]. In ancient Egypt, dyeing was prevalent as an art, and some textiles that were coloured with a natural dye from the madder plant have been found in Egyptian tombs [25]. In modern history, the first synthetic dye to be used was quinine, a drug used to cure malaria that was invented by William Henry Perkin in 1856 [23].

Dyes can be classified in multiple ways. A popular classification is natural and synthetic dyes, while other useful classifications use chemical structures [8] or application methods [11]. Classification by chemical structure involves the functional groups of the molecule’s chromophore such as azo dyes, nitro dyes, anthraquinone dyes, triarylmethane dyes and so forth. Besides this, dyes can also be classified based on their charge upon dissolution in water such as cationic (basic dyes), anionic (direct, acid and reactive dyes), and non-ionic (disperse dyes) [11,26]. Classification of dyes based on their application is often better than their colour nomenclature which is highly complex and with different colour index (CI) numbers [26]. Table 1 shows the classification of dyes based on their application and chemical structure.

Table 1. Classification of dyes based on application and chemical structure

Industrial Application Class	Applications	Chemical Type/Chromophore Structure	Example
Disperse dye (non-ionic)	Polyester, nylon, cellulose, cellulose acetate, acrylic fibres, polyamide, plastics	Azo, nitro, styryl, anthraquinone, benzodifuranone	Disperse Violet 26 (DV26), Disperse Blue 27 (DB27)
Direct dye (anionic)	Paper, cellulose fibres, nylon, rayon, cotton, viscose, leather	Azo, oxazine, thiazole, stilbene, phthalocyanine	Direct Red 28 (DR28), Direct Orange 26 (DR26)
Reactive dye (anionic)	Cellulose fibres, silk, cotton, wool fibres, nylon	Anthraquinone, formazan, oxazine, phthalocyanine, azo, triphenylmethane	Reactive Blue 19 (RB19), Reactive Blue 5 (RB5)
Vat dye (non-ionic)	Cellulose fibres, cotton, viscose, wool	Anthraquinone, Indigoid	Vat Blue 1 (VB1), Vat Blue 4 (VB4)
Basic dye (cationic)	Acrylic, ink, paper, silk, wool, cotton, treated nylon, modified polyester, polyacrylonitrile	Triarylmethane, azo, xanthene, Triphenylmethane, hemicyanine, cyanine, acridine, diazahemicyanine, anthraquinone, oxazine, thiazine	Basic Blue 6 (BB6), MB, MG
Acid dye (anionic)	Nylon, wool, leather, food, silk, cotton, cosmetics, ink-jet printing, paper, modified acrylics	Anthraquinone, xanthene, azo, nitrodiphenylamine, triphenylmethane, nitroso, azine, nitro, indigoid	AO7, Acid Yellow 36 (AY36)

Source: Anisuzzaman et al. [11].

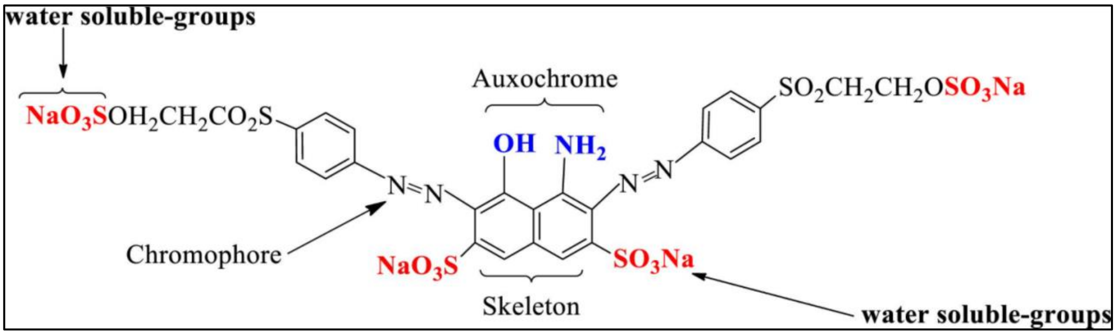

Figure 1. Structure of an azo reactive dye [14]

Table 2. Chemical and Physical Properties of Ozone

Physical Properties	Value
Boiling Point, ºC	-111.9 ± 0.3
Melting Point, ºC	-192.5 ± 0.4
Critical Temperature at 54.6 atm, ºC	-12.1
Evaporation Heat, Kcal/mol	3.63
Dipole Moment, Debye	0.53
Vapor Pressure at -192.5 ºC, mmHg	0.00859
Gaseous Density, g/L	2.1415
Solid Density at 77.4 K, g/cm^3	1.728
Thermal Conductivity at -183 ºC, ºC/cm	0.000531
Dielectric Constant at -183 ºC	4.74

Source: Joseph et al.[32].

Dyes are complex organic molecules that contain two main components namely chromophores and auxochromes. The chromophore is responsible for the colour and is an electron receiver [27]. The chromophore of a dye is capable of absorbing light radiation in the visible spectrum from 380 to 750 nm [14]. The auxochrome helps the molecule to bind to the substance being dyed (affinity function). Acidic groups such as SO_3 and COOH or basic groups such as NH_2, NHR and NR_2 are introduced into the dye structure in order to enhance their solubility [28]. Figure 1 shows an example of the structure of an azo reactive dye.

2. Generation of Ozone and Ozone Properties

Ozone is an unstable gas that can be generated from ambient air or high purity oxygen. It is a powerful oxidant and has been widely used in wastewater or potable water treatment as a detoxifier, decolourizer and disinfectant [29]. Ozone naturally decomposes over time into oxygen due to its instability at ambient temperature and pressure, and does not create secondary pollution in the environment [30]. However, the ozone gas used in the ozonation process must be generated *in situ*, as it is inefficient and dangerous to store ozone gas in large quantities for long periods of time [31]. Ozone may be produced by electrical (corona) discharge, photochemical, radio-chemical and electrolytic methods [32]. The chemical and physical properties of ozone are shown in Table 2.

3. Ozonation Treatment Process

Ozonation is an ozone-based AOP, which uses an indirect pathway of oxidising organics with hydroxyl radicals. It works by utilising the strong, non-selective hydroxyl radical to mineralise chemical compounds contained in organic matter. The hydroxyl radical has a higher oxidation potential (2.80 V) compared to ozone (2.07 V), thus the rate of degradation of the compounds is much faster when hydroxyl radicals are used [32]. Table 3 compares the oxidation potentials of different oxidation agents.

3.1. Reaction Mechanism of Ozone

The ozonation treatment process is pH dependant and involves two different mechanisms, direct reaction and indirect reaction [33]. Oxidation of target pollutants by molecular ozone takes place at acidic pH levels whereas indirect pathways happen in alkaline conditions. The indirect reaction mechanism of ozonation involves various active species with different redox potentials that interact with the target pollutant, such as hydroxyl radicals (2.80 V), superoxide radicals (2.40 V) and hydroperoxide (1.70 V) radicals. These radicals are formed by chain reactions. For the degradation of dyes, the first step of the process tends to be the breakdown of the chromophoric group by reaction with the ozone molecule. Such groups include the azo group or a carbon–carbon double bond connecting aromatic rings [34].

3.1.1. Direct Reaction

The direct reaction of molecular ozone is a selective reaction with a rate constant of 1.0-10^6 $M^{-1}S^{-1}$ [35]. This electrophilic attack usually occurs with atoms such as nitrogen and oxygen, which have a negative charge density and nucleophilic carbons [36]. The general equation for ozonolysis (1) is given below:

$$O_3 + R \rightarrow R_{ox} \qquad (1)$$

Direct ozonolysis tends to occur via two pathways depending on the type of compound, namely 1,3 dipolar cycloaddition or electrophilic reaction. 1,3 dipolar cycloaddition is also known as the Criegee mechanism, shown in Figure 2. This mechanism tends to occur in the presence of a compound containing two unsaturated bonds. Ozone undergoes concerted cycloaddition to cleave the double bond and add the oxygen to the carbon, forming molozonide, which rearranges to form the more stable ozonide. A direct ozone attack occurs at acidic pH (pH < 4) [29]. The primary ozonide formed by bond cleavage is unstable and will decompose into a zwitterion and either an aldehyde or a ketone [32].

The electrophilic pathway tends to occur during ozonolysis of an aromatic compound. This pathway follows two mechanisms. The first is the direct four-centre attack by ozone on the bond exhibiting the strongest double bond character. The second is the electrophilic attack of the outermost oxygen atom of the ozone on the *ortho*-, *meta*-, or *para*-substituent of the aromatic compound [31]. An example of an electrophilic reaction between ozone and an aromatic compound (phenol) is illustrated in Figure 3.

Table 3. Oxidation Agents and their Oxidation Potentials

Oxidizing Agent	Symbol	Oxidation Potential (V)	Relative Potential of Ozone (V)
Fluorine	F_2	3.06	1.48
Hydroxyl Radical	OH	2.80	1.35
Atomic Oxygen	O	2.42	1.17
Ozone	O_3	2.07	1.00
Hydrogen Peroxide	H_2O_2	1.77	0.85
Hydroperoxide radical	HO_2	1.70	0.82
Permanganate	MnO_4^-	1.67	0.81
Chlorine Dioxide	CO_2	1.50	0.72
Hypochlorous Acid	HClO	1.49	0.72
Chlorine Gas	Cl_2	1.09	0.66
Bromine Gas	Br_2	0.87	0.53
Iodine Gas	I_2	0.54	0.26
Oxygen Gas	O_2	0.40	0.19

Source: Joseph et al.[32].

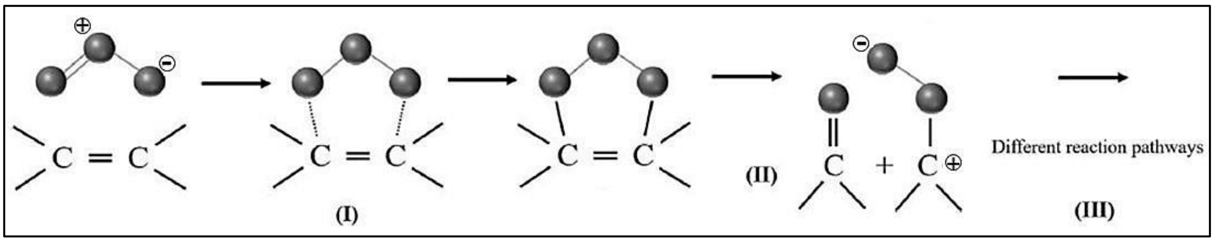

Figure 2. Criegee mechanism of ozone reaction [32].

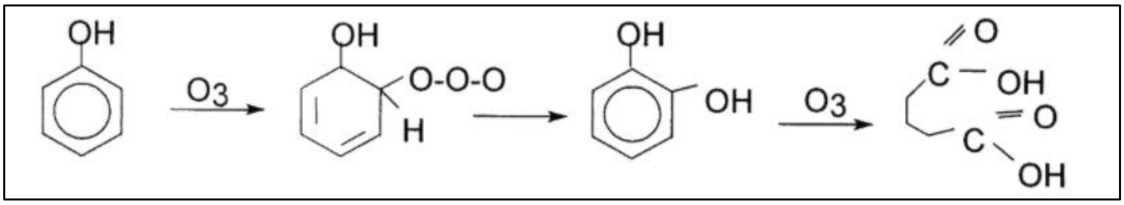

Figure 3. Electrophilic reaction between ozone and phenol [37].

Table 4: Molecular ozone reaction (Direct reaction)

Type of reaction	Target functional group/ molecule	Product
Cycloaddition	Unsaturated compounds (C=C, C=C-O-R)	Carbonyl compounds (aldehydes or ketones) and H_2O_2
Electrophilic reaction	Aromatics substituted with electron donor groups such as -OH, $-NH_2$	Quinoid (e.g. pyridoxine), and aliphatic products with carbonyl and carbonyl functions
Nucleophilic reaction	Molecular sites having electron deficit	Aromatic and aliphatic products

Source: Wang et al. [38]

The overall molecular ozone reactions are summarized in Table 4.

3.1.2. Indirect Reaction

The indirect reaction pathway involves hydroxyl radicals, which are highly unstable and unselective. This mechanism takes place under basic conditions (pH > 8) and is known as ozonation [33]. The radicals degrade organic pollutants primarily through hydrogen abstraction and hydroxylation [36]. The mechanism of reaction can be divided into three steps: initiation, propagation, and termination [35].

a) Initiation

Initiation begins with the decomposition of the ozone molecule by initiators such as hydroxide ions to form a hydroperoxyl radical ($\cdot O_2H$) and a superoxide anion ($\cdot O_2^-$) (2) [35]. The hydroperoxyl radical exists at acid-base equilibrium with the superoxide anion when the pK_a of the solution is 4.8 (3).

$$O_3 + OH^- \rightarrow \cdot O_2^- + \cdot O_2H \qquad (2)$$

$$O_2H \leftrightarrow \cdot O_2^- + H^+ \qquad (3)$$

b) Propagation

This step is also known as the radical chain reaction, where the superoxide anion ($\cdot O_2^-$) formed in the previous step then reacts with more ozone to form an ozonide anion ($\cdot O_3^-$) (4). The ozonide anion is unstable and will immediately decompose to form the hydroxyl radical ($\cdot OH$) (6). The ozonide and the hydrogen trioxide ($\cdot O_3H$) exist in acid-base equilibrium when the pK_a of the solution is 6.2 (5).

$$O_3 + \cdot O_2^- \rightarrow \cdot O_3^- + O_2 \qquad (4)$$

$$O_3H \leftrightarrow \cdot O_3^- + H^+ \qquad (5)$$

$$O_3H \rightarrow \cdot OH + O_2 \qquad (6)$$

i) Hydroxyl Radical Reaction with Ozone

The hydroxyl radical formed can also react with more ozone to form O_4H (7), which decays to form oxygen and a hydroperoxyl radical, allowing the chain to restart (8).

$$OH + O_3 \rightarrow \cdot O_4H \qquad (7)$$

$$O_4H \rightarrow O_2 + \cdot O_2H \qquad (8)$$

ii) Hydroxyl Radical Reaction with Organic Compound

The hydroxyl radical reacts with functional groups in the compound, forming an organic radical ($\cdot R$) (9). If oxygen is present, it can further react with the organic radical to form a hydroxyl radical and continue the chain reaction as given in (10),(11) and (12) [31].

$$H_2R + \cdot OH \rightarrow HR\cdot + H_2O \qquad (9)$$

$$HR\cdot + O_2 \rightarrow HRO_2\cdot \qquad (10)$$

$$HRO_2\cdot \rightarrow R + \cdot O_2H \quad (11)$$

$$HRO_2\cdot \rightarrow RO + \cdot OH \quad (12)$$

c) Termination

Even with an optimal setup, not all radicals will be able to re-enter the chain reaction. This is due to scavenging of the nonspecific hydroxyl radicals by other substances such as degradation products, as shown in (13) and (14). This results in a loss of efficiency, preventing the formation of superoxide radicals while the hydroxyl radicals are gradually used up. Carbonate and bicarbonate ions can act as the scavengers in this scenario [36].

$$OH + CO_3^{2-} \rightarrow CO\cdot_3^{-} + OH \quad (13)$$

$$OH + HCO_3^{-} \rightarrow HCO\cdot_3 + OH^{-} \quad (14)$$

The hydroxyl and hydroperoxyl radicals can also react to terminate the reaction (15).

$$OH + \cdot O_2H \rightarrow O_2 + H_2O \quad (15)$$

4. Developments in Ozonation

Conventional physical, biological, and chemical methods have difficulty in breaking down the chromophores of dyes containing sulphur, nitrogen and various heavy metals. However, ozonation has been successful in targeting and destroying the conjugated chains which impart colour to the molecule [39]. The presence of salts also accelerates the breakdown of dyestuff [34].

In recent years, hybrid processes with ozonation have entered the limelight, showing promising aspects and overcoming common problems encountered during traditional pure ozonation treatment. The reactive oxidative species (ROS) consists of radicals that attack and degrade pollutants, thus many of these novel processes aim to increase the amount of ROS generated during treatment. These hybrid processes include catalytic ozonation, electro-based, photo-based, ultrasound/ cavitation and recently, plasma-based processes. The usage of more niche materials such as carbon aerogel and metal-organic frameworks (MOF) has also been recorded [35]. Meanwhile, new technology such as a moving bed biofilm reactor, rotor-stator reactor (RSR), and the use of contact membranes [40] has been employed as well.

In the studies by Konsowa [41], and Feng and Diao [42], it was found that the ozonation of azo dyes not only successfully removed the colour, but also allowed for further mineralisation by biological methods. In both experiments, the dye was rendered non-toxic after completion of the ozonation process. This allowed the usage of biological methods to further reduce the COD of the wastewater. Normally, dye wastewater cannot be treated using biological methods because it toxic and would kill the organisms used [41,43].

Ozonation tends to suffer from slow dissolution, slow mass transfer and a rapid decomposition rate of the ozone bubbles in the aqueous phase. A novel technology known as microbubbles (MB) is being used in certain setups to mitigate the drawbacks of traditional coarse bubbles (CB) by prolonging the reactivity of ozone in the aqueous phase [35]. These MBs have an average diameter of less than several tens of a micrometre, which allows them to have several favoured properties including higher bubble density, larger surface area, higher inner pressure, and low rising velocity in the liquid phase [44]. All these properties indicate that MB in aqueous solution is much more efficient than standard CB.

The ozonation of CI Reactive Black 5 waste-water was conducted using microbubbles [45], and it was found that the total mass transfer coefficient of MB was 1.8 times higher than for CB. Meanwhile, the pseudo-first order rate constant was 3.2 - 3.6 times higher. This resulted in the total TOC removal in the microbubble system being 1.3 times higher. Improved ozone concentration and more hydroxyl radicals produced during treatment with MB led to increased efficiency.

Zheng et al. found that the gas holdup of MB was higher than for CB, which rapidly increased the saturation of the gas, resulting in an increase of 6.6 times. This was attributed to a higher dissolution ability and higher retention time for MB. The ozone mass transfer coefficient was also found to have increased, as the time used to reach a saturated ozone concentration was halved with the use of MB compared to CB, which improved the dissolution of ozone gas into water [46].

Meanwhile, Wang et al. investigated the use of hollow fibre membranes with UV-ozonation in improving the contact time between the reactive dye Brilliant Red X-3B and ozone. The use of the membrane negated the use of bubbles entirely, focusing instead on the large gas/liquid surface interface; this improved the mass transfer rate overall, which is the primary limiting step in ozonation. Due to the improved transfer rate, the O3 dosage required was thus reduced as well, reducing costs. The membrane contact ozonation (MCO) and UV combined process successfully degraded the dye chromophore, with a COD removal of 90% and TOC removal of 77%. The energy consumption of the process was 4.7 kWh/kg [47].

Another primary challenge faced during ozonation was adjusting the pH during the process. As highlighted previously, the reaction mechanism can proceed by either an indirect or a direct method. The indirect method involves utilising OH radicals to attack the chromophore bonds, and this process is most efficient at a basic pH [41]. The direct method uses molecular ozone to attack the bonds, which is a selective and slower reaction that occurs at acidic pH [35]. Thus, the method chosen must correlate with the pH of the ozonation process.

While the unselective nature and higher oxidation potential of the OH radical is highly favoured, both pathways need to be taken into consideration when planning. Hu et al. found that during a catalytic ozonation process, the colour and COD removal of the Reactive Black 5 dye was greater in alkaline compared to acidic conditions. This was due to the improved decomposition of ozone to hydroxyl radicals, which thus increased the reaction rate [48]. Meanwhile, in a study conducted by Kumar Sonwani et al. where Acid Orange 7 dye was ozonated, they found that the dye removal efficiency was 95 % at pH 3, compared to 64.9 % at pH 11. They concluded that the degradation products may be scavenging hydroxyl radicals, leading to a lower efficiency as the dye was gradually broken down [49]. This was proven by an earlier study conducted by Zhang and Wang, where the addition of carbonate/bicarbonate scavengers would cause the formed hydroxyl radicals to react with them instead of the dye molecules. As the hydroxyl radicals decreased, the oxidation process shifted to a direct reaction instead, using the available molecular ozone [50]. Therefore, pre-treatment assays may be required to investigate the suitable conditions for each dye before carrying out treatment on an industrial scale, as each dye may perform differently at a different pH.

Ozonation can also be enhanced via the use of catalysts. There are two types of catalysts, homogeneous or heterogenous. These serve as a means of increasing the production of OH radicals while decreasing ozone consumption [51]. Homogeneous catalysts consist of metal ions, such as transition metals cations (Cr^{3+}, Mn^{2+}, Fe^{2+}). Heterogeneous catalysts consist of metal oxides, carbons or minerals immobilised on a support [32]. The usage of catalysts can reduce electricity costs, unlike other hybrid methods such as UV which requires additional energy input. While it can be argued that some catalysts are pricey, research has been conducted into the viability of reusing materials as catalysts, such as metal slag. The slag was acquired from metallurgy waste, with the aim of reducing environmental pollution not only in dye wastewater, but also from the catalyst source. This is known as a ‘waste-treats-waste’ approach, allowing ozonation to be approached from a greener perspective [52]. From research conducted on various types of low-cost slag namely Fe-S, Cu-S, Cd-S, Pb-S and Zn-S, the zinc slag was found to be able to effectively decolourise and mineralise Direct Black 22 with a rate of 99% for the former, and 74% for the latter [16].

5. Economic Aspects

During cost-effective analysis, the electrical energy per order (EE/O) indicator tends to be used to study effectiveness. It is defined as the amount of electrical energy (in kWh) required to degrade the pollutant by one order of magnitude in one unit volume (m^3) of contaminated water (16) [53].

$$Electrical\ Energy\ per\ order = \frac{P \cdot t \cdot 1000}{V \cdot log\frac{C_i}{C_f}} \qquad (16)$$

where P is the rated power (kW), V is the volume (L) of contaminated water that is treated at time (t), and C_i and C_f are the initial and final concentrations of the target pollutant respectively (mol/L) [54].

However, this tends to be related to laboratory-scale studies and lacks merit when judging effectiveness on an industrial scale. Thus, industrial effectiveness was studied using real data from an industrial-scale AOP plant located in Poland, namely the ozone dose required during the industrial process (17) [55].

$$\text{Total Ozone Dose} = \frac{\text{O3 dose} \cdot \text{Gas flow rate} \cdot \text{Reaction time}}{Reactor\ volume} \text{(g/L)} \qquad (17)$$

They noted that an ozonation plant tends to have a high investment cost, markedly so when dealing with hybrid processes. Expensive equipment such as UV lamps used in photolysis would significantly increase the cost. However, chemical-based hybrid processes such as O_3/H_2O_2 had a negligible increase in cost. UV-based hybrid processes tended to be around 30% more expensive than O_3 and O_3/H_2O_2 and were thus not recommended for industrial implementation.

This is in line with findings reported by Jiménez et al., where it was noted that ozone-based processes had the lowest energy consumption, while UV and ultrasound had the highest and were still unsuitable for industrial scale implementation when considering efficiency in terms of cost and power. They reported an EE/O value of 188 kW h/m^3 for the ozonation process, followed by 245 kW h/m^3 for photo-Fenton, 505 kW h/m^3 for photo-catalysis, 723 kW h/m^3 for sono-Fenton, and 1634 kW h/m^3 for Fenton reaction at 70 °C [54].

Despite being an effective treatment method, ozonation tends to be expensive when considering the mineralization stage of the chemicals. However, it is cheaper than Fenton processes, since Fenton requires the pH of the wastewater to be adjusted, and the resulting ferric hydroxide sludge requires disposal after the treatment [56].

Hybrid ozonation processes such as UV/O_3 and O_3/H_2O_2 were found to be one to two times cheaper than ultrasound treatments. Labour costs for ozonation were found to be slightly higher than UV and ultrasound treatments due to the increased sampling [57]. According to a study conducted by El-Dein et al., the capital costs for H_2O_2/UV treatment were lower than for the pure ozone-based treatment, however the long-term energy cost required to run UV treatment was more than the ozone production cost. The cost difference in the pre-treatment was estimated to be around €20 per m^3, or approximately RM 99 per m^3 [58].

Thus, the primary cost in ozonation is the amount of electricity consumed. This may be overcome by using alternative energy sources, particularly renewable ones, such as solar energy, geothermal energy or hydrothermal energy. Studies concerning the use of alternative energy in ozonation should be prioritised if this treatment is to be implemented on a larger scale. Another main contributor to the cost is the addition of chemicals such as chlorine or hydrogen peroxide. While mineralisation is improved by the addition of chemicals, ozone pre-treatment alone is enough to degrade the dye chromophores contained in the wastewater.

6. Challenges and Future Perspectives

Ozonation is a competitive and powerful technique compared to conventional treatment methods. The main objectives of dye wastewater treatment by ozonation are: 1) water reuse and recycling, 2) biodegradability improvement of organic substances, 3) disinfection and toxicity reduction and 4) complete mineralisation of recalcitrant or toxic organic substances. Previous studies showed that although ozonation effectively decolourized the organic contaminants present in wastewater, a single ozonation process was often inadequate for complete mineralization of the pollutants due to the low utilization rate and low mass transfer. Complete mineralisation of dye pollutants by molecular ozone is also not economical due to the expensive cost of ozone generation.

During the treatment of dye wastewater by ozonation, the target substance such as the dye residue undergoes a series of oxidation steps which results in intermediate transformation products such as organic acids, some homologues with shorter chain lengths, low molecular weight products, aldehydes and naphthol derivatives or aromatic amines [18,59,60]. Ozone can react more effectively with reactive dyes, but are less effective with non-soluble disperse, vat and sulfur dyes [61]. A toxicity test needs to be conducted to ensure that the intermediate or final products are not more harmful than the parent compounds. An understanding of the degradation mechanisms is crucial for dye degradation and there is still a lack of information on their persistence and ecotoxicity after ozonation treatment.

Single ozonation can be used as a pre-treatment or post-treatment together with conventional methods such as biological and physical treatments. Ozonation alters the molecular structures of the organic substance initially presented in the dye wastewater and improves the biodegradability of the organic pollutants [62,63]. Ledakowicz and co-workers stated that ozonation used after biological treatment was the most recommended method [64]. Its high effectiveness and low energy consumption make this hybrid method very attractive for dye wastewater remediation.

Aside from the direct and indirect reactions of ozonation under basic conditions, there are other ozone-based processes that produce reactive oxidative species, such as a combination of ozone and hydrogen peroxide (O_3/H_2O_2), catalytic ozonation, and a combination of ozone and UV irradiation (UV/O_3). An ozone-based process showed the lowest energy consumption compared with that of UV, ultrasound-based processes, Fenton reaction, etc. [65,66] while energy efficiency in the ozonation process can be achieved using renewable energy sources such as solar, geothermal or hydrothermal energy. The efficiency of ozonation can be improved by hybrid processes and the addition of catalysts, referred to as catalytic ozonation. Hybrid ozone-based processes including UV/O_3 and O_3/H_2O_2 etc. were found to be cost effective compared to ultrasound processes. Despite this, there are still many promising avenues of research within this field, particularly when dealing with the efficiency of industrial-scale studies and the usage of renewable energy.

Compared to single ozonation, catalytic ozonation gives enhanced mineralisation in terms of COD removal efficiency and shorter reaction times. Recent studies follow the direction of utilizing various catalysts in the form of modified materials or composites, such as metals, metal ferrites, metal oxides on supporters, and metal-organic frameworks, to examine their efficiency in the treatment of dye wastewater. In addition, various operational parameters such as temperature, pH, initial concentration, ozone dosage, reaction time and catalyst dosage need to be optimised. The use of optimization techniques such as response surface methodology (RSM) [67], which allows the optimum utilization of ozone, removal efficiency of contaminants and operation cost, is suggested as future research.

CONCLUSION

Dye wastewater need to be treated before being discharged into the environment, particularly into water bodies. Ozonation has been successfully used to decolorize dye wastewater, both as a pre-treatment and a primary method of treatment, and can serve as a promising alternative to conventional methods. The field of ozonation is constantly developing, and many new areas of interest have emerged, such as the usage of microbubbles, renewable waste catalysts and membrane interfaces, among others. The upgrading of a single ozonation process to other ozone-based processes has helped to improve efficiency in terms of degradation of dyes by the production of various active species such as hydroxyl radicals, superoxide radicals and hydroperoxide radicals, as well as cost effectiveness. Current ongoing research with ozonation shows promising results in the removal of dyes from wastewater and reduction of mutagenicity of dye-containing wastewater. With proper utilization of renewable energy resources, ozonation processes may indeed become the future of wastewater treatment.

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