Research on the Advanced Oxidation Technology Based on Dyeing Waste-Water Treatment

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Abstract. Dye waste-water is one of the main sources of water environmental pollution, which belongs to the characteristics of refractory organic waste-water with large chroma, high concentration, large water quality difference, complex composition and large history of pH change. Physical, chemical and biological methods are the main methods on the treatment of dyeing waste-water. The advanced oxidation technology based on hydroxyl radical (•OH) has the advantages of strong oxidation, low selectivity and high electrophilicity. There are mainly seven ways to produce hydroxyl radical (•OH): Fenton oxidation, photo-catalytic oxidation, ozone oxidation, electrocute-chemical oxidation, ultrasonic oxidation, wet oxidation and super-critical water oxidation. These methods have significant effect on dyeing waste-water treatment.

1. Introduction
With the continuous development of social economy, the country’s various industries, especially the rapid development of industry, produced serious industrial waste-water pollution. In industrial waste-water, which is from pharmaceutical, pesticide, dyestuff, chemical, paper, metallurgy, tannery and other industries, is called refractory waste-water because of their complex composition, high concentration, toxic or harmful characteristics [1]. Textile printing and dyeing is not only one of the earliest traditional industries with international competitiveness, but it is a typical high energy consumption and high-water consumption industry. The discharge of printing and dyeing waste-water has been in the front line of the total discharge of industrial waste-water [2,3], which is the main source of refractory organic waste-water. According to the Dye Index, there are more than 7,000 dyes and pigments, of which more than 2,000 are commonly used. Most of the dye production process is complex, the process flow is long, the side reaction is many, the pollutant discharge is large, and the renewal is fast [4]. Printing and dyeing waste-water is mainly produced in various stages of dye production, including the pretreatment process of waste-water desizing, cooking, bleaching, mercerizing waste-water; As well as dyeing waste-water, finishing waste-water, etc. . According to statistics, the annual discharge of textile waste-water in China is about 2.37×10⁹ tons, accounting for 12% of the total discharge of industrial waste-water in China, of which printing and dyeing waste-water accounts for 80% [5].

With the continuous improvement of the requirements of economic sustainable development, the discharge standards of printing and dyeing industry have been improved accordingly, and the traditional dye waste-water treatment methods have become more and more difficult to meet the new environmental standards. Therefore, the development and use of low cost, practical, safe and efficient
dye waste-water treatment technology has important practical value and practical significance for the healthy and sustainable development of printing and dyeing industry and the safety of water environment.

2. Characteristics, hazards and treatment of printing and dyeing wastewater
The summary is shown in Table 1.

| No. | category | contents                                                                 | Literature examples |
|-----|----------|---------------------------------------------------------------------------|---------------------|
| 1   | characteristics of dyeing waste-water | (1) large chroma and high concentration. (2) water quality varies greatly. (3) complex ingredients. (4) the pH value changes greatly. | [5], [6] |
| 2   | harm of dyeing waste-water | (1) destroying the self-purification of waste-water. (2) biological toxicity. (3) cannot be biodegraded. (4) containing harmful contents. | [7], [8] |
| 3   | treatment methods of dyeing waste-water | (1) physical methods. (2) chemical methods. (3) biological methods. | [9], [10], [11], [12] |

2.1. Characteristics of dyeing waste-water
In order to meet the diversified needs of products, printing and dyeing projects usually choose different kinds of processes, which leads to the extremely complex composition of dye waste-water, in which the content of refractory organic matter is high, the biodegradability is poor, and even has a certain toxicity. Dye waste-water usually has the following characteristics [6]:

(1) Large chroma and high concentration. In order to ensure the effect of printing and dyeing, especially silk, hemp and other difficult fabrics, printing and dyeing process often need to add excessive dyes and additives and other substances. most of the organic matter in the dye waste-water is composed of aromatic groups such as benzene, naphthalene, anthracene and quinone as the parent body. the dye waste-water contains a large number of this substance, which leads to its dark color and high concentration of organic matter.

(2) Large variation in water quality the diversity of dye products, at the same time in the process of printing and dyeing, the different stages of the process need to add different dye and additives composition. Therefore, the waste water discharged by printing and dyeing enterprises is basically a mixture of various substances. This leads to the same dye waste-water, whose character is remarkably different and difficult to treat by conventional means.

(3) Complex components. more and more dye varieties, and towards the direction of anti-photolysis, anti- heat and anti- bio-oxidation, make the composition of waste-water more and more complex, often lead to conventional waste-water treatment technology after the dye waste-water treatment cannot meet the discharge standards.

(4) Large variation in pH. In order to improve the coloring rate, it is usually necessary to color the product under different conditions, because the pH of the waste-water also changes with the fabric. Generally speaking, the printing and dyeing process needs to be carried out under alkaline conditions, so the resulting waste-water usually has higher pH.

2.2. Harm of dyeing waste-water
The rich and colorful products enhance the economic benefits of the printing and dyeing industry and accompany the difficult-to-treat printing and dyeing waste-water. The main harm to the environment is as follows [7], and seen in above Table 1:

(1) The dye in the water can absorb light, reduce the transparency of the water body, muddy the water body, and consume most of the oxygen needed by aquatic organisms, resulting in the destruction
of the biological structure of the water body and the disruption of the biological balance, thus destroying its self-purification.

(2) The dyes are aromatic organic compounds, and the hydrogen on the benzene ring is easily replaced to produce a variety of highly toxic poly-benzene ring organic substances, which have certain biological toxicity.

(3) Dye waste-water usually contains heavy metals such as chromium, lead and mercury, which cannot be biodegradable. These heavy metal salts can exist in the natural environment for a long time, spread through the food chain and accumulate in the human body, endangering health.

(4) The composition of organic matter in printing and dyeing waste-water is complex and high, most of which are harmful substances [8]. Even though acid, alkali, salt and other substances or cleaning agents have little impact on ecological security, more and more compounds containing nitrogen and phosphorus have been used in detergent synthesis, and urea has also been used in various printing and dyeing processes to increase the total phosphorus and total nitrogen content in waste-water, resulting in eutrophication problems after discharge.

2.3. Treatment methods of dyeing waste-water

2.3.1. Physical methods. The physical method is mainly to separate or recover the suspended pollutants in the sewage by physical or mechanical action, and transfer them from one medium to another, so as to realize the separation of pollutants. The commonly used physical methods are: Filtration, precipitation, centrifugation, adsorption, extraction, membrane separation and so on. Among them, the adsorption method is the most used, the treatment of printing and dyeing sewage, mainly through the porous of adsorbent, the characteristics of large specific surface area, the adsorption of pollutants to its surface for enrichment, so as to achieve the role of purifying the water body. According to the water quality of printing and dyeing waste-water, we can choose the corresponding adsorbents, such as Liu Dong, etc. novel modified bagasse adsorbents for adsorption of dye congo red (cr). weng et al. [9] used discarded green tea for its adsorption of real dye waste-water [10]. The physical method is simple and easy to operate, but it does not fundamentally change the nature of pollutants, and the treated waste-water still has a considerable pollution effect on the environment.

2.3.2. Chemical methods. Chemical methods mainly through a series of chemical reactions, including: adding chemical reagents, applying light, electricity, microwave and other ways to change the structure or properties of pollutants, has never achieved the purpose of degradation of waste-water. generally can be divided into: chemical reduction method and chemical oxidation method [11]. The reduction method is mainly by adding reducing material to make the pollutant dechlorination and reduction, so as to achieve the purpose of waste-water treatment. Compared with the reduction method, the chemical oxidation method has a broader application prospect, among which the advanced oxidation technology has become a hot research spot because of its strong oxidation ability and high treatment efficiency.

2.3.3. Bio-methods. Biological method or bio-remediation, mainly using the metabolism of microorganisms themselves to decompose organic matter into CO$_2$ and H$_2$O, so as to achieve the effect of degradation of waste-water. According to the different types of microorganisms, they are divided into anaerobic biological method and sunny biological method, usually using aerobic anaerobic combination to treat waste-water. The biological treatment method has simple operation, no secondary pollution, good sludge settling performance, and is widely used in municipal sewage treatment [12]. However, biological methods require high water quality, especially for high toxicity and high concentration of organic waste-water, its biochemical performance is poor, biological methods cannot effectively deal with this kind of waste-water.
3. Application of advanced oxidation technology in dyeing waste-water treatment

The summary is shown in Table 2.

Table 2. Application of advanced oxidation technology in dyeing waste-water treatment.

| No. | category                  | contents                                                                                     | Literature examples |
|-----|---------------------------|----------------------------------------------------------------------------------------------|--------------------|
| 1   | Fenton oxidation          | Hydroxyl radical mechanism reaction mechanism.                                                | [13], [14]         |
|     |                            | The method of oxidizing and decomposing organic and inorganic pollutants in waste-water by photoexcited oxidation-reduction reaction using semiconductor as catalysts. | [15], [16]         |
| 2   | Photocatalytic oxidation  | Strong oxidizing substance •OH was generated, and its strong oxidizing property was used to degrade organic matter. | [17]               |
| 3   | Ozone oxidation           | Electron transfer is carried out directly with the electrode, or •OH radical is generated through anodic reaction to further degrade pollutants in waste-water. | [18], [19]         |
|     |                            | Under the action of ultrasonic field, the tiny bubbles existing in the liquid will oscillate, grow, collapse and close, etc. The generated energy will accelerate the speed of chemical reaction and cause acoustic solution, thus promoting the decomposition of organic matter. | [20]               |
| 4   | Electrocatalytic oxidation| In the liquid phase at high temperature (125~320 ℃) and high pressure (0.5~10 MPa), oxygen (or ozone, hydrogen peroxide, etc.) is used as oxidant to oxidize and decompose organic pollutants in the liquid phase. | [21]               |
| 5   | Ultrasound oxidation      | In supercritical state, organic pollutants and oxidants (air, O₂ and hydrogen peroxide, etc.) undergo homogeneous oxidation reaction in oxygen-rich supercritical water, thus degrading organic pollutants. | [22], [23]         |
| 6   | Wet oxidation             |                                                                                               |                    |
| 7   | Supercritical water oxidation |                                                                                               |                    |

3.1. Fenton oxidation

Fenton oxidation is the earliest and most widely studied advanced oxidation method. In 1894, the French scientist Fenton published the discovery of the rapid oxidation of tartaric acid by mixing Fe²⁺ and H₂O₂ in acid solution. In memory of this scientist, the Fe²⁺/H₂O₂ mixed reagent was called Fenton standard reagent and the reaction using this reagent was called Fenton reaction [13]. For the mechanism of Fenton reaction, it is generally accepted that the mechanism of hydroxyl radical reaction proposed by Haber and Weiss [14] is as follows in Formula (1)-(4):

\[
\begin{align}
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (1) \\
Fe^{2+} + OH & \rightarrow Fe^{3+} + OH^- \quad (2) \\
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + H^+ + H_2O_2 \cdot \quad (3) \\
H_2O_2 + H_2O_2 \cdot & \rightarrow O_2 + H_2O + \cdot OH \quad (4)
\end{align}
\]

From the above reaction process, it can be seen that what actually acts as oxidation in Fe²⁺/H₂O₂ system is the hydroxyl radical oh produced by Fe²⁺/H₂O₂ reaction, which has high oxidation activity,
which can degrade organic pollutants in water. In addition, Fe$^{3+}$ can regenerate Fe$^{2+}$ by reaction with H$_2$O$_2$. Although the Fenton method has the advantages of quick reaction speed, easy operation and easy generalization, there are also some defects, such as: Short time of •OH in water leads to its low utilization rate, pH must be kept in acid condition to ensure the reaction proceed, Fe$^{2+}$ cannot be reused, H$_2$O$_2$ is difficult to store and transport many problems. To solve the above defects, people are constantly investigating how to improve the traditional Fenton system. Zepp et al [15] found that illumination can effectively accelerate the oxidation degradation rate of pollutants in the Fenton reaction. In addition to the introduction of illumination, other researchers have introduced electricity, microwave, ultrasound into the classical Fenton system, which achieved considerable results. All methods are collectively referred to as Fenton-like oxidation methods.

3.2. Photo-catalytic Oxidation

Photo-catalytic oxidation technology was first discovered by Japanese scientists Fujiyama and Hamada in 1972 [16]. As light source generates energy, UV or visible light causes semiconductor catalysts or oxidants to have the ability to transition to form electron holes with strong oxidizing properties, producing a large number of active substances such as oxygen free radicals and •OH in water to degrade the waste-water. The semiconductor catalysts are mainly TiO$_2$, ZnO, Fe$_2$O$_3$, WO$_3$, CDs and so on, among which TiO$_2$ is nontoxic and cheap, high absorption rate of UV light, good corrosion resistance and chemical stability. Strong oxidation capacity and strong adsorption capacity to many organic pollutants and other advantages, becoming a common material in photo-catalytic oxidation technology. Although the photo-catalytic oxidation method is low in cost, it requires high transparency of water body. How to improve the light utilization and industrial application is a hot research topic.

3.3. Ozone Oxidation

Ozone (O$_3$) is a strong oxidant and is usually used for sterilization, disinfection, decolorization, deodorization. Because of the strong oxidation of ozone, it has also been used in water pollution treatment in recent years, and its reaction mechanism with organic matter can be divided into direct reaction and indirect reaction [17]. The direct reaction is mainly with unsaturated aliphatic compounds, unsaturated aromatic compounds, and some special functional groups. The reaction has certain selectivity and low efficiency; The indirect reaction is that ozone produces strong oxidizing substance •OH under the action of alkali, light or other factors to degrade organic matter using its strong oxidation performance.

The ozone oxidation method is easy to operate and the reaction conditions are mild, but the ozone treatment waste-water alone still has such defects as low O$_3$ utilization, insufficient oxidation capacity and low O$_3$ content. Therefore, the current research focus is to develop joint technology to further improve its degradation efficiency.

3.4. Elector-chemical Oxidation

According to the difference of its reaction mechanism, elector-chemical oxidation can be divided into two oxidation modes: Elector-chemical direct oxidation and elector-chemical indirect oxidation. Elector-chemical direct oxidation is the degradation of organic contaminants in waste-water using high potential oxidation of the anode. During the reaction, the contaminants are transferred directly to the electrodes; whereas elector-chemical indirect oxidation is the degradation of contaminants in water by strong oxidants such as •OH radicals through the anodic reaction [18-19]. The specific reaction processes are as follows in Formula (5)-(9):

$$\text{MO}_x + \text{H}_2\text{O} \rightarrow \text{MO}_x(\bullet\text{OH}) + \text{H}^+ + \text{e}^- \quad (5)$$

$$\text{MO}_x(\bullet\text{OH}) + \text{R} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- + \text{MO}_x \quad (6)$$

$$\text{MO}_x(\bullet\text{OH}) \rightarrow \text{MO}_{x+1} + \text{H}^+ + \text{e}^- \quad (7)$$
\[ R + \text{MO}_{x+1} \rightarrow \text{RO} + \text{MO}_x \]  
\[ \text{MO}_{x+1} \rightarrow \frac{1}{2}\text{O}_2 + \text{MO}_x \]  

3.5. Ultrasonic Oxidation

Ultrasonic technology for the degradation of organic matter is not the direct action of ultrasonic on organic matter molecules, but the degradation of organic matter through ultrasonic cavitation. Ultrasonic cavitation refers to the behavior of oscillation, growth, collapse and closure of tiny bubbles present in liquid under the action of ultrasonic field. The energy generated by this behavior process can accelerate the rate of chemical reaction and cause acoustic solution, then promote the decomposition of organic matter [20]. The mechanism of ultrasonic wave action is mainly to use the sound wave with frequency of 15 kHz to 1.0 MHz to directly pyrolysis the organic matter and produce the oxidant under the instantaneous high temperature and high pressure in the tiny region. Removal of organic matter by per-oxidation.

3.6. Wet Oxidation

Wet oxidation method refers to a pollution treatment technology in which organic pollutants in liquid phase are oxidized and decomposed by oxygen (or ozone, hydrogen peroxide, etc.) in high temperature (125~320℃) and high pressure (0.5~10 MPa) liquid phase [21-22]. Under suitable temperature and pressure conditions, the treatment efficiency is high, and the COD removal rate of wet oxidation method can reach more than 90%. The wet oxidation method has a high demand for temperature and pressure [23-24]. In order to overcome the above shortcomings, people are constantly studying and improving the method. Catalytic Wet Air Oxidation (CWAO): Addition of Combination to Traditional Wet Oxidation Reactions suitable catalyst, reducing the activation energy required for the reaction, so that the reaction can be carried out under more mild conditions, reducing the reaction time, and also being able to make the oxidation process more thorough by changing the reaction course, thus avoiding the formation of toxic intermediate by-products [25-26].

3.7. Super-critical Water Oxidation

When the temperature and pressure of the water in the environment are above its critical value (374 °C, 22.1 MPa), the water will be in a new fluid state which is different from both gaseous, liquid and solid, super critical state, and the water in this state is called super-critical water. The principle is to degrade organic pollutants and oxidants (air, O₂, hydrogen peroxide, etc.) by homogeneous oxidation reaction in oxygen-enriched super-critical water under super-critical state. Super-critical water has some unique properties: Non-polar organic matter, O₂, N₂ can be dissolved in any proportion in super-critical water.

4. Conclusions

As a dye wastewater difficult to biodegrade organic wastewater, it has the following characteristics: large chroma, high concentration, large difference in water quality, complex composition, large pH value change. The main treatment methods include: physical method, chemical method and biological method. Fenton oxidation method, photocatalytic oxidation method, ozonation oxidation method, electrochemical oxidation method, ultrasonic oxidation method, wet oxidation method and supercritical water oxidation method constitute the methods of producing hydroxyl radical (•OH). Advanced oxidation technology based on hydroxyl radical (•OH) has the advantages of strong oxidation, low selectivity, high electrophilicity and so on.

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