Treatment Technology of Difficult-Biodegradable Printing and Dyeing Waste-Water

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Abstract. The pollution of printing and dyeing waste-water mainly comes from dyes. In the process of printing and dyeing, different dyeing processes produce different pollutants, resulting in the difference of their properties. The treatment of printing and dyeing waste-water, according to the difference of technical principles, mainly includes seven treatment technologies: physical method, biochemistry method, physical chemistry method, ozone oxidation method, Fenton reagent oxidation method, photocatalytic oxidation method and wet (catalytic) oxidation method. Different treatment methods are used for waste-water with different properties and concentrations. Biochemical decomposition of organic matter in waste-water by microbial metabolism is a common method for the treatment of printing and dyeing waste-water.

1. Introduction
With the rapid development of industry, the problem of water environment pollution is becoming more and more serious. At present, water environmental pollution is one of the most urgent problems facing all countries in the world [1]. In particular, the development of pharmaceutical, chemical, dye and other industries, making high concentration of refractory waste-water more and more, their treatment has become a major difficulty in waste-water treatment [2], such waste-water is characterized by high toxicity of pollutants, mainly containing aromatics compounds such as aniline, nitrobenzene, etc; high concentrations of pollutants can COD up to hundreds of thousands of mg per litre. BOD5/ COD generally less than 0.1, difficult-biodegrade, such waste-water treatment methods research is one of the hot issues of concern [3-4].

In the field of water treatment, compared with advanced oxidation technology, biotechnology has advantages in treatment cost, technical difficulty, operation management and so on, which is favored by the vast number of water handlers. However, biotechnology can only treat waste-water with better biodegradability, and for organic waste-water with refractory biodegradation, biotechnology shows great limitations [5]. Therefore, combining biological basis and advanced oxidation technology, the treatment of organic waste-water has the advantages of low treatment cost and wide application range.

2. Main components of dyeing waste-water
The main components of printing and dyeing waste-water are from dyes, which are throttled in sewage after dyeing cloth, or during cleaning. For printing and dyeing enterprises, due to their different
processes and different water quality of the waste-water produced, the water quality of each process of printing and dyeing [6] is generally shown in Table:

| Waste water types          | waste-water characteristics                                                                 |
|----------------------------|---------------------------------------------------------------------------------------------|
| Retrograde waste-water     | Degrating is to hydrolyze the paste on the fabric into soluble substances by chemical agents and then remove it. The water quantity is small, but the pollutant concentration is high, which contains various kinds of slurry, slurry decomposition, fiber chip, starch alkali and various auxiliaries, which makes the waste liquid alkaline, the pH value is about 12, and the COD_{Cr} and BOD_{5} are very high. |
| Cooking waste-water        | The amount of water is large and the concentration of pollutants is high, which contains cellulose, fruit acid, waxy, oil, alkali, surfactant, nitrogen-containing compounds, etc. The cooking waste-water is dark brown, alkaline is very strong, and the water temperature is high. |
| Bleaching waste-water      | Bleaching is the removal of cotton, hemp fiber on the natural pigment, make the fiber white. Its waste water is large, but the pollution is light, it contains residual bleach, a small amount of acetic acid, oxalic acid, sodium thiosulfate and so on. |
| Mercerizing waste-water    | The alkali content is high, the NaOH content is 3%~5%, most printing and dyeing plants are recovered by evaporation concentration NaOH, so mercerized waste-water is generally rarely discharged, and the waste-water discharged after alkali recovery is still strong alkaline, and the pH value is as high as 12~13, and the COD_{Cr}, BOD_{5}, SS is very high. |
| Dyeing waste-water        | The quantity of water is large, and the water quality varies with the different dyes used, which contain slurry, dyes, auxiliaries, surfactants and so on. The waste-water is generally alkaline and has a high chromaticity. For the dyeing waste-water of vulcanized and vat dyes, the pH value can reach more than 10. The COD_{Cr} value is higher, the BOD_{5} value is lower, and the biodegradability is poor. |
| Printing waste-water       | It mainly comes from the washing waste-water of color matching sizing, printing drum and screen, as well as the flower washing water after printing, soap washing liquid and so on. The amount of water is large, the concentration of pollutants is high, and the waste water contains a large amount of slurry in addition to dyes and auxiliaries. COD_{Cr} and BOD_{5} are high, of which the BOD_{5} value accounts for about 15% and 20% of the total COD_{Cr} and BOD_{5} value in printing and dyeing waste-water. |

Printing and dyeing waste-water has the characteristics of complex composition, high content of refractory organic pollutants (up to 50,000 mg/L), high chromaticity, high chemical oxygen demand (COD_{Cr}), high biochemical oxygen demand (BOD_{5}), large alkalinity, and high toxicity, large quantity of water and large change of water quality. If it is consumed by animals or absorbed by plants, toxic and harmful pollutants will also accumulate in animals and plants and are not easily discharged. Printing and dyeing waste-water also contains a variety of biological toxicity or lead to "three causes " (carcinogenic, teratogenic, mutagenic) organic matter, has been a difficult point in industrial sewage treatment, but also the current domestic and foreign water pollution control needs to be solved.
3. Treatment Technology of Printing and Dyeing waste-water

3.1. Technical overview

It is found that the waste-water has the characteristics of high concentration, high color and difficult-biodegradation. Due to the development of chemical fiber fabric in recent years and the development of finishing technology after printing and dyeing, PVA dyes, new additives and other difficult-biodegradable organic matter into the printing and dyeing waste-water in large quantities. Because of the large change of raw materials, high alkalinity, rapid and drastic change of water quality, a large part of dyes and pigments are difficult to biodegrade macromolecular substances, the colored groups should not be destroyed firmly, so the traditional biological decolorization treatment process is facing new challenges. In response to the above problems, new biological treatments are concentrated at home and abroad process, efficient decolorizing bacteria, new chemical agents, advanced oxidation technology exploration and application research. Among them are representative anaerobic-aerobic biological treatment process, high-efficiency special decolorizing bacteria and PVA degradation decolorizing bacteria and PVA degradation enzymes, development of high-efficiency decolorizing coagulant, application of advanced oxidation technologies such as photocatalysis, ozone oxidation and wet oxidation, membrane separation technology and popularization and application of cleaner production process. The treatment technology of printing and dyeing waste-water is shown in Table [7].

Table 2. Treatment technology of printing and dyeing waste-water.

| No. | classification       | The technology principle                                                                 | Cases            |
|-----|----------------------|----------------------------------------------------------------------------------------|------------------|
| 1   | Physical law         | Using physical techniques including filtration, precipitation, adsorption, air floatation and membrane separation | [8]-[16]         |
| 2   | Biochemical methods  | Treatment of organic matter in waste-water by microbial metabolism including aerobic and anaerobic biological processes | [17]-[19]       |
| 3   | Physical-chemical process | Using a combination of physical and chemical techniques, including chemical and electrocoagulation | [20], [21]      |
| 4   | Ozone oxidation      | The chemical bond of unsaturated chromophore group in printing and dyeing waste-water was opened by oxidizing agent ozone to produce small molecular weight to achieve the purpose of decolorization | [22]            |
| 5   | Fenton reagent oxidation | Oxidants H₂O₂ react with reducing Fe²⁺ ions to produce strong oxidizing free radicals HO⁺, make dye molecules break bonds and decolorize. | [23]            |
| 6   | Photocatalytic oxidation | an oxide semiconductor luminescence excitation is used to generate electron/hole pairs, and the hole acts with the aqueous phase to form HO⁺, thereby oxidizing colored pollutants | [24]            |
| 7   | Wet (catalytic) oxidation | Under high temperature and high pressure conditions, organic matter and inorganic reducing substances dissolved or suspended in waste-water are oxidized into CO₂ and H₂O treatment methods in liquid phase | [25]-[29]       |

3.2. Physical principle

The physical methods commonly used in the treatment of printing and dyeing waste-water are filtration, precipitation, adsorption, air floatation and membrane separation. Bentonite, as adsorbent and flocculant in water treatment, has been widely used in the field of decolorization of printing and dyeing waste-water. In order to further improve the treatment effect, a variety of composite bentonite
[8], VS fiber [9] and polystyrene-based cation exchange fiber [10] have the functions of physical adsorption and ion exchange, and have better decolorization effect than surface, fast ion exchange rate, easy regeneration and difficult to treat cationic dye waste-water. Some adsorbents that integrate adsorption and flocculation properties such as diatomite composite water purifiers have also been developed [11]. The modified fly ash with flocculation properties is made from fly ash in electric plants, which has a high decolorization rate for both hydrophobic and hydrophilic dye waste-water [12]. Air flotation method is one of the commonly used process water purification methods. Fu Yan Primary [13] reported the use of hexadecyltrimethylammonium bromide as a collector to treat reactive dyes in printing and dyeing waste-water by ion flotation and discussed the flotation mechanism. Zhang Hongwei et al. [14] reported the application of air floatation filtration method to the treatment of dyeing waste-water in washing workshop of a textile factory in Tianjin Status.

Membrane separation is the use of membrane micropores for filtration, the separation of suspended solids from the water in printing and dyeing waste-water, so that the water quality can be purified, and its osmotic solution can be reused to reduce the waste of water resources [15]. At present, ultrafiltration membrane technology is the most widely used, which uses the extremely fine pores in the film to filter larger molecules, which can reduce the chemical oxygen demand, biochemical oxygen demand and suspended solids in waste-water [16]. Compared with traditional chemical treatment, this method can reduce the use of chemicals and can operate continuously. Membrane separation is used to remove insoluble dyes (e.g. disperse dyes). The water quality is clean after filtration can be reused, but the method is not ideal for soluble dyes.

### 3.3. Biochemical methods

Waste-water biochemical treatment is the treatment method of decomposing organic matter in waste-water by the metabolic action of microorganisms [17]. The treatment time of aerobic biochemical method is short, and the nitrification time required by anaerobic biochemical method is long, so the anaerobic-aerobic combination process, or the typical process flow of adding biochar and chemical flocculant after it [18-19]. This process is aimed at some polymer substances with poor biodegradability in printing and dyeing waste-water, and it is expected that they will be hydrolyzed and acidified in the anaerobic section to become small molecular substances, thus creating conditions for the aerobic section. In addition, the excess sludge produced by the aerobic stage is returned to the anaerobic stage for anaerobic nitrification, which makes the whole sludge system without excess sludge discharge. As a follow-up process of aerobic treatment of biochar or condensation precipitation and other physicochemical methods, the effluent quality has played a role in ensuring.

### 3.4. Physical chemical process

Printing and dyeing waste-water generally contains a large number of particle suspensions. Chemical condensation method [20] and electrocoagulation method [21] are usually used in the treatment process. Broad-spectrum and high-efficiency coagulants are the focus of chemical condensation. It is generally believed that for water-soluble dyes, the main decolorization effect is the adsorption of colloidal substances and tiny flocs produced by coagulation, and at the same time, the flocculants formed also intercept the fine suspended matter by bridging, electric neutralization. At present, some new coagulants with good decolorization effect on dyes are often reported, but various coagulants have no universality for decolorization of dyes, and a large number of chemical pollutants produced bring secondary pollution.

### 3.5. Chemical oxidation

For the treatment of printing and dyeing waste-water, the oxidation method can degrade the difficult-biochemical organic matter in a short time, the treatment efficiency is high, and does not produce secondary pollution, so it has been paid more and more attention by researchers. The oxidation method can be divided into ozone (O₃) oxidation, Fenton reagent (H₂O₂/Fenton) oxidation, incineration,
photocatalytic oxidation and catalytic oxidation according to the different oxidant and oxidation conditions.

1. Ozone oxidation method: Ozone can open the chemical bond of unsaturated chromophore group in printing and dyeing waste-water, and produce substances with small molecular weight to achieve the purpose of decolorization. Ozone oxidation [22] has a fast decolorization rate and good effect on water-soluble dyes such as reactive dyes, cationic dyes, acid dyes and direct dyes. The treatment effect of hydrophobic dyes such as disperse dyes, vat dyes and sulfur dyes is poor and the amount of ozone is large.

2. Fenton reagent oxidation method: in the decolorization treatment of dyes, H$_2$O$_2$ is also a frequently used oxidant, H$_2$O$_2$ the oxidation ability is weak when used alone, and the oxidation ability is enhanced when coexisting with Fe$^{2+}$ ions. The decolorization mechanism is that H$_2$O$_2$ react with Fe$^{2+}$ ions to produce strong oxidizing free radicals, make dye molecules break bonds and decolorize. Moreover, because Fe$^{2+}$ ions have both coagulation, the removal of dyes from waste-water by Fenton reagents is very effective [23]. The disadvantage of this method is that Fe$^{2+}$ ions will promote H$_2$O$_2$ decomposition, the oxidation efficiency of H$_2$O$_2$ is not high, and the reaction is not high and it needs to be carried out under the condition of pH 3, so the treatment of printing and dyeing waste-water by this method still needs to consume a lot of acid, resulting in new pollution sources and equipment corrosion.

3. Photocatalytic oxidation: under light conditions, multiphase semiconductor photocatalysts completely oxidize organic matter to form CO$_2$ and H$_2$O, semiconductor catalysts, such as ZnO, TiO$_2$, Fe$_2$O$_3$, Cu$_2$O, CdS and ZnS. Photocatalytic oxidation is the use of an oxide semiconductor luminescence excitation to produce electron/hole pairs, and the formation of holes acting with the aqueous phase, thereby oxidizing colored pollutants. A lot of researchers have used photocatalytic oxidation to treat printing and dyeing waste-water, and achieved good results, the treated water quality reached or close to the "textile dyeing and finishing industry water pollutant discharge standard "((GB42) 87-92) The first-level criterion[24]. But most of the current studies use mercury lamp, xenon lamp as light source, the photocatalytic efficiency is not high, and when used repeatedly, the catalytic activity is greatly reduced, which directly limits the application of photocatalytic oxidation. Photocatalytic treatment of printing and dyeing waste-water by sunlight instead of artificial light source is a developing direction. At present, the main research of photocatalytic oxidation is how to improve the photocatalytic efficiency and how to use solar light.

4. Wet (catalytic) oxidation: The treatment of organic and inorganic reducing substances dissolved or suspended in waste water and oxidized to CO$_2$ and H$_2$O in the liquid phase by wet oxidation through oxygen or air at high temperatures and pressures. Chen et al. [25] carried out wet air oxidation removal using a high pressure reactor at a temperature of 413~573 K, a partial pressure of oxygen of 1.69 MPa. The results show that thermal decomposition plays a significant role in the removal and the COD of oxidation removal increased with the increase of temperature. Yang Runchang et al. [26] the wet oxidation of the simulated azo dye methyl orange solution was catalyzed under pressure conditions, and the decolorization rate of the treated water samples reached more than 95%. Dhale[27] and Zhang Zhongyan et al. [28] used homogeneous CuSO$_4$ and heterogeneous Cu/η-Al$_2$O$_3$ catalysts to treat dye waste-water, and the COD removal rates reached 90% and 77%, respectively; Lin et al. [29] treated desizing waste-water with CuSO$_4$ catalyst, and the removal rate reached more than 80%. However, the loss of homogeneous Cu catalysis increases the cost and brings secondary pollution. The loss of single component Cu/η-Al$_2$O$_3$ catalyst in Cu use is serious, which shortens the service life of catalyst and brings secondary pollution.

4. Conclusion
Dye is the main component of dyeing waste-water pollution. Different printing and dyeing processes produce different pollutants. According to the different technical principles, the treatment methods of printing and dyeing waste-water, mainly including physical method, biochemistry method, physical chemistry method and other 7 treatment technologies, different properties of waste-water treatment
methods. Among them, the biochemical method is an economical and practical common method for the treatment of printing and dyeing waste-water.

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