Pollution and Treatment of Dye Waste-Water

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Abstract. With the rapid development of industry, the production of dye waste-water has increased year by year. Dye composition complex, high concentration, and high color, difficult to biodegradable substances, difficult to biodegrade. According to the chemical structure, dyes are mainly divided into eight categories, such as azo dyes; according to the application can be divided into 14 categories, such as reactive dyes, acid dyes and so on. Dyes show chroma contamination due to the presence of chromophore and chromophore in the molecular structure. Dye waste-water comes from dyestuff industry, printing and dyeing factory, wool spinning factory and other industrial enterprises. The treatment methods of dye waste-water include physical method, chemical method and biological method, among which biological method is economical and practical.

1. Introduction

In recent years, the dye industry has been rapidly developed. According to the United States" Color Index", commodity dyes have reached tens of thousands. About 60,000 tons of dyes are discharged into the environment in the form of waste each year worldwide [1], 80% of which are azo dyes.

In China, dye industry is an important part in textile, light industry, chemical industry and other fields. According to the data published by the National Bureau of Statistics, at present, China's fuel production and trade volume are ranked first in the world [2], of which 70-80% are azo dyes. According to the Technical Policy on Prevention and Control of waste-water Pollution in Printing and Dyeing Industry, issued in 2001," according to incomplete statistics, the amount of waste water discharged by textile industry is as high as 900 million tons per year, accounting for the sixth place in industrial discharge ". In these printing and dyeing waste-water, the dye composition is complex, high concentration, high color, difficult to biodegrade substances are many [3], and contain a variety of organics with biological toxicity and three properties (carcinogenic, teratogenic, mutagenic), so it is often difficult to achieve the desired effect by using a single treatment technology. For example, the traditional biological treatment has the problems of low processing efficiency and even unable to run, while the physical and chemical treatment has the disadvantages of high processing cost, small processing capacity and harsh operating conditions. Therefore, it is urgent to develop a new treatment process which is effective for this kind of waste-water so that it can meet more and more stringent discharge standards and achieve the purpose of comprehensive treatment. Applying CWO technology to the treatment of dye waste-water, especially azo dye waste-water, has great environmental significance, theoretical significance and practical application value.
2. Material composition of dye waste-water

2.1. Types of dyes

The structure of dyes is complex and various. According to the third edition of the Dye Index, there are more than 5,000 varieties of dyes with different chemical structures, of which more than 1,500 have been published [4]. There are about 500 kinds of dyes produced in China [5-6].

Dyes are generally classified according to the two methods of application and chemical structure [7]. For the convenience of application, the names of commercial dyes are mostly classified according to the application of dyes, while the classification by chemical structure directly represents the characteristics and commonness of dye structure. According to the chemical structure classification, dyes are mainly divided into eight categories: azo dyes, anthraquinone dyes, indigo dyes, phthalocyanine dyes, sulfur dyes, Jia Chuan dyes, triaryl methane dyes, heterocyclic dyes. According to the application classification, dyes are mainly divided into fourteen categories: reactive dyes, acid dyes, direct dyes, insoluble azo dyes, vat dyes (refers to insoluble), soluble vat dyes, sulfur dyes, acid mordant dyes and acid medium dyes, oxidation dyes, polycondensation dyes, disperse dyes, basic dyes and cationic dyes, fluorescent dyes, fluorescent brighteners. Among them, neutral dyes and cationic dyes are two kinds of dyes which are singled out from acid dyes and alkaline dyes, respectively.

Acid dyes, reactive dyes, cationic dyes, alkaline dyes, direct dyes, vector dyes and neutral dyes are water-soluble dyes; among them, acid dyes, reactive dyes, cationic dyes and basic dyes have a higher solubility in water, and the solubility of direct dyes, vector dyes and neutral dyes is slightly poor; ice dye, disperse dyes, vat dyes and sulfur dyes are generally insoluble in water.

The molecular structure of reactive dyes contains reactive groups, which can form covalent bonds with hydroxyl groups on cellulose fibers, protein fibers and amine groups on polyamide fibers under appropriate conditions, and combine into a "dye-fiber" whole, so reactive dyes are also called reactive dyes. With the continuous adjustment and development of the product structure of textile printing and dyeing industry at home and abroad, the domestic demand for dyes is also expanding year by year, especially reactive dyes, and the output has exceeded 20% of the total amount of dyes in the world. In 2004, the total production of reactive dyes in China exceeded 110000 tons, an increase of 25.6% in the same proportion as the previous year.

The reason why reactive dyes have such a large proportion is that compared with other cellulose fiber dyes, it has the advantages of complete chromatography, bright color, excellent fastness to washing, simple application process, convenient use and applicability, relatively cheap price, and its structure does not contain carcinogenic aromatic amines and so on. At present, reactive dyes have been able to replace some ice dye, sulfur dye and vat dye, but also suitable for the printing and dyeing needs of cellulose fiber products, which makes it more widely used.

Although reactive dyes have many of the above advantages, they also have the following disadvantages: (1) Low utilization. General utilization rate is only 60%~70%, producing a large amount of colored sewage, its chromaticity is more than a few thousand times, and the concentration of organic matter is high. (2) High electrolyte consumption during dyeing. This not only increases the labor intensity, but also causes the increase of chloride ion concentration in the waste-water, which increases the difficulty of dye waste-water treatment. (3) The amount of nonferrous waste-water containing salt is large and difficult to treat. (4) The colour fastness of certain types of dyes does not meet market requirements.

2.2. Dye color theory

There have been a variety of explanations for dye hair color theory. The theory of "chromophore" is put forward, and it is believed that the chromophore of organic compounds is due to chromophore groups containing double or triple bonds, such as azo-nitro-nitro-nitro-nitro- NO2, NN=N-, O, so on. Aromatic hydrocarbons containing chromophores are called chromophores. The molecules of organic compounds, as dyes, also contain "chromophore ", such as amino- NH2, hydroxyl- OH, carboxyl-COOH, which can strengthen the role of chromophore. Although the above theory is only an induction
of phenomena, the concepts of chromophore and chromophore are still widely used. Chromophore refers to the dye π bond conjugation system, and chromophore refers to the polar group connected to the conjugate system which can increase the maximum absorption wavelength and molar absorbance.

Light has fluctuations and particle duality [8]. Light is a stream of particles consisting of many particles called light quanta or photons. Photons have a certain amount of energy, have the following relationship with the speed of light, the frequency of light and the length of light. See Formula (1):

$$E = hv = \frac{hc}{\lambda}$$  \hspace{1cm} (1)

In the form: $E$- photon energy (10⁻⁷J),

$h$- Planck constant (6.62×10⁻³⁴ J•s),

$v$- Frequency (s⁻¹),

$c$- The speed of light (3×10¹⁷nm/ s),

$\lambda$- Wavelength (nm).

From the above formula, the energy of light is proportional to the frequency of light and inversely proportional to the wavelength of light. Light waves of different wavelengths have different energies.

3. Source and characteristics of dye waste-water

3.1. Sources of dye waste-water
waste-water discharged by the dye industry, including dye production, and the mixing of various waste-water produced by the reprocessing of natural and man-made fiber materials by printing and dyeing plants, wool spinning plants, knitting plants, silk factories, etc. Printing and dyeing processing generally includes pretreatment (desizing, refining, bleaching, mercerization), dyeing, printing, finishing and other four processes [9]. The pretreatment stage (including the process of firing, desizing, boiling, bleaching, mercerizing, etc.) should discharge the desizing waste-water, cooking waste-water, bleaching waste-water and mercerizing waste-water, dyeing process discharge dyeing waste-water, printing process discharge printing waste-water and soap liquid waste-water, finishing process discharge finishing waste-water. Printing and dyeing waste-water is a mixture of the above kinds of waste-water, but the main source of printing and dyeing waste-water is dyeing waste-water.

3.2. Properties of dye waste-water
Because dyeing engineering all use water as medium, and often need one or more times of water washing, so the water consumption is relatively large. The water quality of waste-water discharged from various processes varies greatly from fiber type, dye and slurry. Because of the complex types of dyes, the waste-water mainly contains impurities such as dyes, pastes, auxiliaries, oil agents, acid and alkali, fiber and inorganic salts, and its chemical composition is benzene, naphthalene, anthraquinone, etc. The composition of printing and dyeing waste-water produced when various dyes are used [10] as shown in Table 1:
Table 1. Components of various printing and dyeing waste-water.

| Types of dyes             | Main Contamination Components in waste-water                      |
|---------------------------|-------------------------------------------------------------------|
| Direct dye                | Dyes, Ming powder, salt, soda, surfactant                         |
| Reactive dye              | Dyes, caustic soda, sodium phosphate, baking soda, meta powder, urea, surfactant |
| Acid dye                  | Dyes, Ming powder, ammonium sulfate, acetic acid, sulfuric acid, surfactant |
| Acid mordant dye          | Dyes, acetic acid, meta-powder, dichromate, surfactant            |
| Metal complex dye         | Dyes, sulfuric acid, sodium acetate, ammonium sulfate, meta powder, surfactants |
| Cationic dye              | Dyes, sodium acetate, soda, ammonium acetate, surfactants         |
| Primulin bases            | Dyes, Sulphur Alkali, Soda, Metamine                              |
| Vat dye                   | Dye, caustic soda, insurance powder, meta powder, red oil         |
| Disperse dye              | Dyes, caustic soda, hydrochloric acid, sodium nitrite, sodium acetate, surfactants |
| Coating material          | Pigments, ammonia, sodium alginate, resins, mineral oils          |

4. Treatment of dye waste-water

4.1. Technical overview

Basic raw materials for dye production are benzene series, naphthalene series, anthraquinone, aniline and benzidine compounds, and in the them are chelated with metals, salts and other substances during the production process, resulting in dye waste-water mostly containing salt, chloride or bromide, microacid or alkali, metal ions, sulfur containing high chemical oxygen demand (COD), high color, "tri-induced "toxic refractory organic waste water [11-12]. Common treatment techniques for dye waste-water are shown in Table 2.

4.2. Physical principle

Because the ratio of Five-day-biochemical oxygen demand (BOD₅) and determination of COD by potassium dichromat (CODₜₐ) is less than 0.4 and the biodegradability is poor, the salt content in the waste-water will further reduce the biodegradability of the waste-water [13], so the physical method is often used as the pretreatment method of dye waste-water to facilitate the recovery of dye molecules from the waste-water, reduce the content of salt and metal ions, and increase it Biochemical. The physical methods used in the field of dye waste-water treatment include: adsorption method [14], membrane separation technology [15] and magnetic separation [16].

4.3. Chemical methods

Chemical methods mainly include electrochemical method and advanced oxidation method. Electrochemical methods have high energy consumption, high cost and electrode storage disadvantages in side reactions such as oxygen evolution and hydrogen evolution [17]. In recent years, researchers have developed many new electrode materials. New high oxygen evolution overpotential electrodes and high hydrogen evolution overpotential electrodes have emerged in electrooxidation and electroreduction, which improve the treatment effect and provide another reasonable choice for the treatment process of dye waste-water. Electrochemical methods can be divided into electrochemical reduction and electrochemical oxidation [18], electrocoagulable electrical floating [19] and so on. Advanced oxidation technology is a new water treatment technology in recent years. Hydroxyl radicals (·HO) with strong oxidation can be produced during the treatment of this technology. Organic molecules that can stabilize many structures and even be difficult to decompose by microorganisms, are converted into non-toxic and harmless biodegradable low-molecule substances, the reaction end products are mostly carbon dioxide, water and inorganic ions, and no excess sludge and concentrate are produced [20].
Table 2. Common treatment techniques for dye waste-water.

| No. | Classification | Technical essential | Superiority | Scope of application | Problems |
|-----|----------------|---------------------|-------------|----------------------|----------|
|     | Physical law   | Adsorption method   | ---         | Waste utilization, simple operation | Water soluble dyes, cationic dyes | Poor regeneration of adsorbent and small adsorption capacity |
|     | Membrane technology | --- | The decolorization effect is obvious | Disperse dyes | High cost of membrane clogging |
|     | Chemical methods | Electrochemical process | Electrochemical Oxidation and Electrochemical Reduction | The processing color, COD, BOD and TSS are effective, the process is flexible and adaptable | Dyes other than cationic dyes | High unit power consumption, high iron consumption and high cost |
|     |                 | Electric Coagulation Electrical Floatation | Electric Coagulation Electrical Floatation | Low investment, large handling capacity, hydrophobic dye, high decolorization efficiency | Disperse dyes, vat dyes, sulphur dyes | Low decolorization ability for hydrophilic dyes, low COD removal efficiency, chemical sludge production, secondary pollution |
|     | Advanced Oxidation Method | Photo-catalytic oxidation | The catalyst input is small, the treatment effect is good, the reaction time is short | --- | High catalyst price and reuse problem, low utilization of light energy and complex reactor |
|     | Fenton and Class Fenton Oxidation | O3 oxidation | Fenton reagents have both oxidation and coagulation effects | --- | The process condition is harsh, the running cost is high, the excess sludge is produced more |
|     | Bio-analysis | Aerobic Method | --- | Economy | --- | Long processing time, unstable effect, impact resistance |
|     | Anaerobic process | --- | Decolorization effect is good, residence time is short | --- | Produce a large amount of aniline, the effluent biological toxicity increased |
|     | Anaerobic/aerobic process | --- | High COD removal rate, good economy | --- | Poor impact resistance, poor adaptability, reaction time |

4.4. Biological law
Compared with chemical oxidation with high energy consumption and high cost, biological treatment is favored by many industrial waste-water treatment processes because of its economy. The commonly used biological treatment methods mainly include aerobic biological treatment [21], anaerobic
biological treatment [22] and aerobic and aerobic facultative biological treatment [23]. In the treatment of dye waste-water, anaerobic degradation and aerobic degradation have their own pertinence.

5. Conclusion
The production of dye waste-water develops rapidly with the development of modern industry. Dye waste-water is difficult to biodegrade because of its complex composition, high concentration, high color and many difficult biodegradable substances. Dye fraction classification, according to the chemical structure is mainly divided into azo dyes and other eight categories, according to the application can be divided into reactive dyes, acid dyes and other 14 categories. Because the molecular structure contains chromophore group, the dye shows that the color forms chromaticity pollution. the composition of dye waste-water varies due to different properties of dyes. Physical, chemical and biological methods are common treatment methods for dye waste-water, among which biological methods are economical and practical.

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