Advanced Approaches in Dyeing and Printing Wastewater Treatment: A Comparative Study of Physical and Chemical Methods

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Abstract: This thesis presents a comprehensive analysis of various physical and chemical methodologies for treating dyeing and printing wastewater, which is a significant environmental concern in the textile industry. It delves into physical techniques like ultrafiltration, nanofiltration, reverse osmosis, and magnetic separation, evaluating their efficiency in removing contaminants and the challenges faced, such as membrane fouling and the requirement for high-quality magnetic seeds. The study also explores chemical methods like electrochemical oxidation and photocatalytic oxidation, highlighting the advancements in electrode materials and the use of TiO2 catalysts in degrading pollutants. A comparison is made between the effectiveness, operational constraints, and economic viability of these methods, emphasizing the need for optimizing existing technologies and developing hybrid systems that integrate the strengths of individual techniques. This research aims to contribute to the ongoing efforts on enhancing wastewater treatment efficiency, reducing environmental impact, and promoting sustainable practices in the textile industry. This work serves as a reference for future research on wastewater treatment, offering insights into developing more effective, cost-efficient, and eco-friendly solutions.

Keywords: Dyeing and printing wastewater treatment; Nanofiltration; Electrochemical oxidation; Photocatalytic oxidation

1. Introduction

China is one of the countries with the scarcest water resources per capita in the world. Its freshwater resources per capita are only a quarter of the world’s average, ranking 110th globally. The country is characterized by significant temporal and spatial variations in water distribution, a mismatch between water and soil resources, and a relatively fragile ecological environment. As socioeconomic development continues, the water demand is constantly increasing, exacerbating the imbalance between China’s water scarcity and socioeconomic development. The annual discharge of textile wastewater in China is about 2.37×10^9 tons, of which 80% is from dyeing and printing. The treatment of dyeing and printing wastewater is challenging. Moreover, the reuse rate of wastewater after treatment is only about 10% [1]. Therefore, in-depth research on the treatment and reuse of
wastewater is essential to alleviate the increasingly concerning water scarcity issue in China.

2. Dyeing and printing wastewater

Dyeing and printing wastewater refers to the wastewater discharged during the textile dyeing and printing processes. Some enterprises discharge all production wastewater (including direct and auxiliary production wastewater), while others include some domestic wastewater in their discharge, causing constant fluctuations in water quality. Therefore, the water quality of dyeing and printing wastewater often varies [2]. Generally, dyeing and printing wastewater is characterized by significant changes in water quality, high content of organic pollutants, high alkalinity, deep color, and large differences in pollutants. Overall, dyeing and printing wastewater is a type of organic wastewater containing some dye and difficult-to-degrade substances. Currently, dyeing and printing wastewater in China are treated with conventional secondary treatment, which is primary physicochemical treatment followed by biochemical treatment. However, due to the varying water quality of dyeing and printing wastewater and the continuous elevation of related standards, conventional secondary treatment can no longer meet the high standards for discharge and reuse. This is because the effluent from conventional secondary treatment contains a high amount of dye and residues of difficult-to-degrade substances (mostly organic compounds with a molecular weight of less than 1000), such as chlorobenzene, xylene, acetophenone, naphthalene, and phenanthrene [3]. These substances are toxic, difficult to degrade, and prone to accumulation, posing direct threats to the environment and human health.

3. Physical methods for treating dyeing and printing wastewater

3.1. Adsorption method

The adsorption method involves using porous solids to remove one or several substances from wastewater. Activated carbon is widely used in the deep treatment of dyeing and printing wastewater. It is a non-polar adsorbent known for its resistance to strong acids and alkalis and its ability to withstand water immersion, high temperatures, and high pressure. Furthermore, it demonstrates good adsorption performance and chemical stability, making it a popular choice for wastewater treatment. Adsorbents are selective, so research on this method emphasizes finding cost-effective adsorption materials. This has been a subject of continuous research by scholars both in China and internationally. The main adsorbents used in the treatment of dyeing and printing wastewater are described below.

(1) Natural minerals that can perform electrostatic adsorption through lattice substitution, surface termination, or ion exchange adsorption, are used for decolorization in dyeing and printing wastewater. This method has an efficacy of more than 90%.

(2) Natural polymers such as sugar, chitin, and protein that are chemically modified can be used for the decolorization of dyeing and printing wastewater. The abundance of these natural polymer materials and the significant increase in their dye adsorption capacity after modification make them a cost-effective method of waste treatment.

(3) Hydrolyzed protein is an amphoteric protein that can be obtained from chicken feathers, duck feathers, hooves, and other proteins. It can also be obtained from the sericin in the wastewater of silk degumming. Hydrolyzed protein not only has a good dye adsorption capacity but can also be chemically modified to enhance its adsorption capacity for ionic or nonionic dyes.

(4) Coal slag is also a cost-effective wastewater treatment method. Activated coal and sulfonated coal, which are made from the byproduct of coal combustion, are considered potential tools for wastewater treatment.
treatment due to their porous structure, large surface area, and high reactivity. Furthermore, their inherent microbial oxidation properties prevent the production of sludge sediment \[^4\].

3.2. Membrane separation method

The membrane separation method mainly involves the separation of particles through a selective membrane, which is used in the pretreatment of dye wastewater. This method separates dye molecules from water molecules and allows the recovery of dye molecules and salts. Besides, it enhances the biodegradability of the wastewater. This process is purely physical and does not alter the molecular structure of the dyes.

3.2.1. Ultrafiltration and nanofiltration

Due to the complexity of dyeing wastewater, which often has a high salt content, the membrane separation method is limited by the rapid flux decline caused by membrane fouling. Therefore, researchers often use a combination of nanofiltration and ultrafiltration to treat dyeing wastewater.

In a study, an integrated process of ultrafiltration/nanofiltration was used to deeply treat the effluent from secondary biological treatment of dyeing wastewater. In the study, they compared the effectiveness of three different types of ultrafiltration membranes with varying materials and molecular weight cut-offs as pretreatment methods for nanofiltration. Two industrialized nanofiltration membranes were selected to study the effects of pressure and operational time on the separation performance of the two membranes and to analyze changes in the structure of different material membranes before and after treatment. The results showed that ultrafiltration membranes as a pretreatment for nanofiltration effectively removed 90% of turbidity and some chemical oxygen demand (COD). Therefore, this concludes that nanofiltration can effectively remove various salts in the wastewater and facilitate the recovery of dye \[^5\].

3.2.2. Reverse osmosis

Reverse osmosis membranes can effectively remove both electrolytes and non-electrolytes with a relative molecular mass greater than 300. The removal rate for substances with a relative molecular mass between 100 and 300 is over 90%. The permissible operating pH range for this method is 2 to 11. Since the relative molecular mass of dye molecules in dye wastewater is generally around 1000, and the pH value is between 3 and 10, reverse osmosis membranes should technically be able to retain dye molecules. Thus, reverse osmosis can be a feasible method for treating dyeing wastewater. Research has been done on the treatment of wastewater from Fuyang Textile Printing and Dying Factory using an integrated reverse osmosis device. The treatment effect was evaluated based on three indicators: COD removal rate, electrical conductivity, and color. The results showed that using reverse osmosis to treat dye wastewater at an operating pressure of 1.5 MPa, the effluent electrical conductivity was 23 μS·cm\(^{-1}\), the COD removal rate reached 99.5%, and the color was reduced from 4500 times the original water to 7 times \[^7\].

3.3. Magnetic separation

The magnetic separation method is a physical separation method that separates substances according to their magnetic properties. This method mainly utilizes the coagulability of pollutants and the addition of magnetic seeds. Coagulability refers to the agglomeration of ferromagnetic or paramagnetic pollutants into larger particles under a magnetic field to remove them from water; seeding involves the use of magnetic seeds (magnetic powder) to enhance the magnetic properties of weakly paramagnetic or non-magnetic pollutants for easier removal by magnetic separation. The pollutants in dyeing and printing wastewater are usually weakly magnetic or diamagnetic, so they cannot be directly separated by magnetic forces. Therefore, it requires the addition of
magnetic seeds and coagulants into the water. Furthermore, due to the presence of water-soluble pollutants in dyeing and printing wastewater, the direct addition of magnetic seeds and coagulants makes it difficult for the pollutants to bind to the seeds. Therefore, it is necessary first to alter the solubility characteristics of the pollutants so that they can be removed through magnetic separation.

A study has been done on treating dyeing and printing wastewater with a color intensity of 800 times and a COD of 565.0 mg·L\(^{-1}\) with low-dose Fenton oxidation followed by magnetic seed coagulation and high-gradient magnetic separation. The study showed that adding more magnetic powder did not necessarily result in better performance (the best effect was observed with 150 mg·L\(^{-1}\) of magnetic powder). When the amount of magnetic powder reached 150–200 mg·L\(^{-1}\), the removal rates of color and COD tended to plateau, reaching 92.6% and 79.5% respectively, which meets the national secondary emission standards. Low-dose Fenton reagents can reduce the water solubility of organic matter, which facilitates coagulation. Ferromagnetic materials not only improve coagulation and flocculation but also serve as good adsorbent materials. They can also be easily separated using magnetic separation techniques, facilitating the effective recovery and reuse of the adsorbents.

4. Chemical methods

4.1. Electrochemical method
Electrochemical reduction removes environmental pollutants through cathodic reduction. This method can be divided into direct and indirect electro-reduction. Electrochemical oxidation on the other hand involves the removal of pollutants through the anode or oxidants produced at the anode, which can also be categorized into direct and indirect electrochemical oxidation. In the electro-oxidation process, the main side reaction is anodic oxygen evolution due to water electrolysis; in the electro-reduction process, it is the hydrogen evolution reaction. The electrodes are the core of electrochemical water treatment technology and have been highlighted in dye wastewater treatment processes in recent years.

A research team conducted comparative degradation experiments on the azo dye methyl orange using mixed metal oxide electrodes and boron-doped electrodes. The effects of current density, electrolyte type, pH, and initial pollutant concentration on the removal of color, COD, and TOC from dye wastewater were examined. The results showed that pollutant degradation behavior differed between the two types of electrodes. The boron-doped electrode had a broader applicability for dye wastewater treatment compared to the mixed metal oxide electrode. From an economic perspective, the boron-doped electrode is a better choice for dye mineralization\[^8\].

Another research team used a TiO\(_2\) nanotube photoelectrocatalytic (PEC) reactor to treat dye wastewater. The treatment of rhodamine B wastewater using a TiO\(_2\) nanotube electrode was investigated and the performance of the PEC reactor was compared with that of a traditional photocatalytic reactor. The treatment effects of anodized TiO\(_2\) nanotube electrodes and TiO\(_2\) sol-gel electrodes on rhodamine B were also studied. In the experiment, 20 mg·L\(^{-1}\) rhodamine B was treated for 180 minutes. The results showed that the performance of the anodized TiO\(_2\) nanotube was 30% higher than that of the sol-gel TiO\(_2\) electrode. Further research indicated that the inclined thin-film PEC reactor had better treatment effects on dye wastewater than the TiO\(_2\) sol-gel electrode due to improved mass transfer efficiency\[^9\].

4.2. Photocatalytic oxidation method
The photocatalytic oxidation method was initiated in 1972 and has since been progressively applied in various fields. Using photocatalytic oxidation to treat dyeing and printing wastewater is a novel and promising method. Common methods include TiO\(_2\)/UV, H\(_2\)O\(_2\)/UV, and O\(_3\)/UV.
A research team used an open-type suspended photocatalytic reactor and replaced ultraviolet lamps with solar ultraviolet radiation. After 2 hours of solar radiation, the decolorization rate of the cationic blue X-GRRL dye wastewater was between 80% and 90% \[^{10}\].

Another research team conducted experiments on the photocatalytic degradation of rhodamine dyes in wastewater using a flat-plate photocatalytic reactor coated with a thin layer of TiO\(_2\). The results showed that the concentration of rhodamine dye in wastewater decreased from 10 mg·L\(^{-1}\) to 0.01 mg·L\(^{-1}\) \[^{11}\].

This technology boasts several outstanding advantages, such as low energy consumption, ease of operation, no secondary pollution, and complete mineralization of organic substances. However, it also has drawbacks, including long reaction times, high costs, low efficiency and recovery of the catalyst, short lifespan, and low efficiency of UV lamps.

### 5. Conclusion

This thesis has explored various methods for treating dyeing and printing wastewater, focusing on their effectiveness and challenges. It covered physical techniques like ultrafiltration, nanofiltration, reverse osmosis, and magnetic separation, alongside chemical methods such as electrochemical and photocatalytic oxidation. Physical methods, especially ultrafiltration and nanofiltration, effectively remove contaminants, while reverse osmosis excels in reducing electrolytes in wastewater. Magnetic separation, though innovative, faces challenges like the need for high-quality magnetic seeds. Chemical methods, particularly electrochemical oxidation, have advanced with the emergence of new electrode materials that improve pollutant degradation. Photocatalytic oxidation using sunlight and TiO\(_2\) catalysts offers an eco-friendly option but struggles with long reaction times and catalyst recovery. Each method has its advantages and limitations, with physical methods often constrained by operational demands and chemical methods by efficiency and cost. Optimizing these techniques and developing hybrid systems that combine their strengths is crucial for the future of wastewater treatment. The enhancement of treatment efficiency is vital for the textile industry, which is a major contributor to global water pollution.

The findings from this thesis provide a foundation for future research in wastewater treatment, indicating the need for more effective, economical, and environmentally friendly solutions.

### Disclosure statement

The author declares no conflict of interest.

### References


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