Progress Research on Treatment Methods of Printing and Dyeing Wastewater

Yuchao Chen¹, Yiming Zhang¹, Yuhang Yuan¹, Haixiang Li¹,²*, Kun Dong¹ and Xiangmin Li¹

¹ Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guilin University of Technology, Guilin, Guangxi, 541006, China
² State Key Laboratory of Pollution Control and Resource Reuse Research, Tongji University, Shanghai, 200092, China
* Corresponding author’s e-mail: lihaixiang0627@163.com

Abstract. With the rapid development of the printing and dyeing industry, the amount of wastewater discharged is also increasing. Printing and dyeing wastewater is recognized as one of the most difficult industrial wastewater treatments due to its complex composition, high content of refractory organic matter, high chroma, high alkalinity and poor biodegradability. This paper mainly reviews the characteristics and effects of the advanced oxidation method (Fenton oxidation method, photocatalytic oxidation method, ozone oxidation method, wet oxidation method, electrochemical oxidation method) for treating printing and dyeing wastewater, a preliminary outlook on the combined use of several methods was also carried out.

1. Introduction
Printing and dyeing wastewater mainly includes wastewater such as de-sizing wastewater, scouring wastewater, bleaching wastewater and mercerized wastewater[1]. As the world's largest textile printing and dyeing country, printing and dyeing wastewater is a major wastewater discharge in China, which has a great impact on the ecological environment and human health. According to the 2015 Annual Report on Environmental Statistics, among the 41 industrial sectors surveyed and reported, the discharge of printing and dyeing wastewater ranks in the top four, reaching 1.84 billion tons[2]. For a long time, printing and dyeing wastewater has become a difficult point in the field of industrial wastewater treatment due to its high concentration of refractory organic matter, high alkalinity and high chroma[3,4]. Due to the variety of dyes and complex composition, with the introduction of “Water Ten” and related laws, the requirements for industrial wastewater discharge are increased, and the traditional printing and dyeing wastewater treatment methods are seriously challenged, and it is difficult to meet the emission requirements[5]. Therefore, development of economical and efficient printing and dyeing wastewater treatment methods has become the focus of the wastewater treatment industry. Based on the above situation, this paper focuses on several advanced oxidation methods that are currently used, and a preliminary outlook for the new joint treatment methods.

2. Fenton oxidation
Fenton oxidation is an advanced oxidation method using H₂O₂ as an oxidant and a ferrous salt as a catalyst. Under acidic conditions, hydroxyl radicals generated in the reaction can rapidly oxidize pollutants[1,3,4] in wastewater. Compared with other methods, Fenton oxidation has the characteristics...
of mild reaction conditions (usually carried out under normal temperature and pressure), low operating cost, simple process and high processing efficiency. However, since ferrous ions can be stably present in an acidic system, the Fenton reaction usually needs to be carried out under acidic conditions, which imposes some restrictions on the use of Fenton oxidation [3,6].

Xu Zeng et al. [7] used Fenton oxidation method to study the printing and dyeing wastewater of a factory, and explored the effects of wastewater pH, reaction time and dosage on COD removal. The results show that under the optimal process conditions (The pH of wastewater is 3, the reaction time is 40 min, the dosage of ferrous sulfate is 1250 mg/L, and the dosage of 30% hydrogen peroxide is 1.5 g/L), and the COD removal rate of wastewater reaches 80%. Ping Yao [8] used the homogeneous Fenton method to treat printing and dyeing wastewater, and discussed the effects of reaction temperature, reaction time, reaction temperature, solution pH and Fe²⁺/H₂O₂ concentration ratio on the treatment effect. Under the optimal reaction conditions (reaction temperature is room temperature, reaction time is 30~40 min, solution pH is 3~5, Fe²⁺/H₂ concentration ratio is 1:5~1:10), COD The removal rate is above 70%, and the removal rate of chromaticity can reach 100%.

3. **Photocatalytic oxidation**

Photocatalytic oxidation is the oxidation of water by catalyst (titanium dioxide, hydrogen peroxide, iron oxalate [4]) under the action of ultraviolet light or visible light [3]. It is a new catalytic technology with oxidation ability. Strong, mild reaction conditions and wide application range. However, due to the characteristics of the pollutants in the printing and dyeing wastewater, the reaction process is prone to produce toxic by-products, which may cause secondary pollution. In addition, the catalyst performance degradation and recovery problems also limit the application of the method to some extent.

Peiyao Xu et al. [9] carried out photocatalytic degradation experiments on frozen yellow G dye, using nano-TiO₂ as catalyst, the removal rate of COD after UV light treatment for 6 h was 80%, and the removal rate of chroma was as high as 98.5%. With the continuous development of materials science, researchers are constantly exploring new catalysts to improve the processing effect. Guangyou Wang et al. [10] used graphene as a novel photocatalyst to study the removal effect of photocatalytic oxidation on methylene blue printing and dyeing wastewater. It was found through experiments that the optimum conditions (graphene dosage 2.68 mg, solution pH 12, wastewater) At an initial mass concentration of 19.34 mg/L, the degradation rate of methylene blue reached 100%. Suresh, P. et al. [11] studied the synergistic effect of nano-nickel oxide-loaded activated carbon as a photocatalyst for the degradation of printing and dyeing wastewater. The results show that under the irradiation of ultraviolet light, nano-nickel oxide-loaded activated carbon has stronger light than pure nickel oxide. Absorption capacity and better charge separation ability, the treatment effect is greatly improved.

4. **Ozone oxidation**

Ozone oxidation is the use of ozone in different catalysts [6] (CeO₂, CuO, MnFe₂, Fe₂O₃, MnO₂ and MgO [14-15]), of which manganese dioxide has high catalytic activity, and magnesium oxide is a non-toxic, economical and environmentally friendly substance, which is widely used in wastewater treatment [16]. Under the rapid decomposition of ozone to form a strong oxidizing hydroxyl free Base, non-selective oxidative decomposition of organic pollutants in water, which compensates for the selective degradation of organic matter by incomplete ozonation and the incomplete mineralization [12-13]. Ozone oxidation has the advantages of sterilization and deodorization, and obvious decolorization effect. The ozone after treatment is easy to decompose and does not cause secondary pollution, which is in line with the concept of green environmental protection [4].

Sha Zhao et al. [17] found that the ozone decolorization efficiency of the dyeing of the dye of the dye was higher at 40 °C, reaching 99.5%, and the removal rate of COD was also 88%. Yan Yu [18] used ozone oxidation method to deeply treat the secondary biochemical effluent of printing and dyeing wastewater in industrial park. The removal of COD and chromaticity was carried out under the conditions of ozone dosage of 40 mg/L and reaction time of 40 min. The rate is 32% and 75%. Guanghua Chen [19] found in the pilot study on ozone deep treatment of a wastewater treatment plant in a printing and dyeing
industrial park in Guangdong that ozone oxidation has an unstable removal effect on low concentration COD, and the average removal rate is 19%, but the removal efficiency of chromaticity. Relatively good, the average removal rate is 52%. It can be seen from the above studies that the ozone oxidation method has a very significant effect on the removal of chromaticity. In order to optimize the ozone oxidation technology, some researchers set out to study the new type of catalyst. Xiangning Guan et al.[20] used activated carbon fiber (ACF) as carrier to prepare Mg-Mn/ACF catalyst by sol-gel method and used floating bed reaction. The catalytic effluent ozonation treatment of the secondary effluent of the printing and dyeing wastewater and the cationic red X-GRL simulated wastewater, and the effects of different initial pH, catalyst dosage, intake flow rate, O3 content, HRT and other parameters on the treatment effect and the catalyst were investigated. stability. The results showed that under the optimal conditions (pH=8, catalyst dosage 4 g/L, gas volume flow rate 0.9 L/min, O3 mass concentration 40 mg/L, HRT 40 min, reaction run 80 min), COD The removal rate is approximately 80%.

5. Wet oxidation
Wet oxidation method (including wet catalytic hydrogen peroxide (CWPO), wet air (WAO) and other oxidation methods) is used in air at high temperature (125~374 °C), high pressure (0.5~20.0 MPa) and liquid phase conditions. Oxidizing agents such as oxygen to oxidize organic substances in water to inorganic substances such as CO2 and H2O or small molecule organic substances[3-4,21,22] have attracted the attention of researchers in recent years. The method has the characteristics of high speed, high efficiency, thorough reaction and small secondary pollution. The method is still in the experimental research stage in China. Although the efficiency of the traditional high-concentration organic wastewater treatment method is greatly improved, it is usually carried out under high temperature and high pressure, and the equipment requirements are relatively high. Therefore, the actual printing and dyeing wastewater is Applications in processing are subject to certain restrictions.

Lei Luo[23] analyzed the reaction mechanism and advantages of wet catalytic hydrogen peroxide (CWPO) technology. The experimental results show that the method has a good application prospect and application value in the printing and dyeing wastewater treatment process. Shutian Zhou[24] used wet oxidation to treat wastewater with high concentration of azo dye methyl orange. The COD removal rate of wastewater was 85%, and the chroma removal rate reached 99%. Tangjun Lu[25] selected 10 kinds of dyes to simulate printing and dyeing wastewater, and used zeolite as carrier and Cu, La and Mo as metal carriers. Under the optimal ratio and reaction conditions, the catalytic wet oxidation method was used to simulate printing and dyeing wastewater. The removal rate of the blended violet D-BL is over 95%. Ling He[26] studied the degradation of reactive brilliant blue KN-R by wet catalytic hydrogen peroxide (CWPO). If the initial mass concentration of dye is 200 mg/L, under optimal reaction conditions, color and organic carbon (The removal rates of TOC) reached 100% and 68.5%, respectively.

6. Electrochemical oxidation
Electrochemical oxidation is a new type of oxidation technology that has sprung up in recent years. It refers to the direct or indirect oxidative degradation of organic matter in wastewater by electrode (anode) reaction under electrolysis conditions. The mechanism of action is that H2O (acid solution) or -OH (alkaline solution) first discharges hydroxyl radicals on the surface of the anode, and then the O in the adsorbed hydroxyl group is transferred to the MOx lattice to form MOx+1, MOx+1 further undergoes a redox reaction with an organic substance to remove organic contaminants[3,27]. Compared with other treatment methods, the method has the advantages of no need to add redox agent, no secondary pollution, strong controllable reaction, high treatment efficiency and mild reaction conditions.

Zhaoyang Wang et al.[28] used three-dimensional electrocatalytic treatment of steel slag particle electrodes to treat simulated printing and dyeing wastewater. The results show that the three-dimensional electrochemical oxidation system using magnetic steel slag particle electrode degrades rhodamine B in simulated printing and dyeing wastewater with good treatment effect. The optimal conditions (initial mass concentration 5 mg/L, cell voltage 5 V, pH 4) With a supporting electrolyte concentration of 0.15 mol/L, the removal rate of Rhodamine B is close to 90%. Parsa et al.[29] used Ti/Sb-SnO2 as the anode
and stainless steel as the cathode to decolorize the active 7 (RO7) dye wastewater in a batch reactor containing NH₄Cl. Since the current density of Ti/Sb-SnO₂ electrolyte is higher than that of lead and graphite electrode, the strong oxidizing substance ClO⁻ is accelerated by increasing the current, the decolorization rate is 95.3%, and the COD removal rate is 70.3%. Irikura et al.[30] treated the acid green 28 with a Ti/β-PbO₂ anode in a filter press reactor. The effect of different parameters on the decolorization rate was studied by statistical response surface methodology (RSM). When the pH value is 5, the decolorization rate of the wastewater reaches about 90%. Isarainchavez et al.[31] compared the oxidative degradation ability of Ti/Ir-Pb, Ti/Ir-Sn, Ti/Ru-Pb, Ti/Pt-Pd and graphite electrodes. The results show that Ti/Ir-Pb, Ti/Ir-Sn the oxidative degradation effects of Ti/Ru-Pb and Ti/Pt-Pd are better than those of graphite electrodes, and the Ti/Ir-Pb anode has the best decolorization effect. Under the optimal process conditions, the decolorization rate of methyl orange can reach about 96%.

7. Conclusion
As a new and advanced water treatment technology, advanced oxidation technology has the characteristics of fast reaction rate, good treatment effect and wide application range, and has been widely used in the treatment of printing and dyeing wastewater. With the development of today's society, the printing and dyeing industry has also developed rapidly. While people are pursuing high fashion, the processing difficulty of printing and dyeing wastewater has been greatly deepened, and the types of pollutants have become more and more complicated. Although the single advanced oxidation method can effectively treat organic matter and chromaticity, as far as practical applications are concerned, the advanced oxidation method still has many shortcomings in the treatment of printing and dyeing wastewater. In the face of complex pollutants, it is necessary to pay attention to the influence of other pollutants in the treatment process, and also need to consider the equipment, technical requirements, catalyst recovery and energy consumption of various treatment methods.

In today's green environment, the emission requirements for printing and dyeing wastewater are greatly enhanced. Traditional methods using single oxidation are increasingly unable to meet their requirements. In view of this background, many researchers focus on advanced oxidation and other methods. In the exploration of the combined technology, Zongwei Ye[32] used the A/O-Fenton combination technology to increase the COD removal rate to about 90% and improve the removal efficiency. Ling Xu et al.[33] made a new attempt in the treatment of printing and dyeing wastewater by Fenton oxidation + Ca(OH)₂ coagulation combined process. In addition, photo-induced anaerobic and other metaplastic processing technologies are slowly emerging. The continuous improvement of various technologies such as materialization and metaplasia should be the focus of future research, and this is also the call for responding to the national new environmental protection concept.

References
[1] Cai, X.M., Zheng, Y. (2018) Research progress in printing and dyeing wastewater treatment technology. J. Printing and dyeing auxiliaries, 3: 5-8.
[2] Ministry of Ecology and Environment. (2015) 2015 Annual Report on Environmental Statistics. China Environment Press, Beijing.
[3] Kong, S.C. (2019) Research progress in dyeing wastewater treatment methods. J. China Resources Comprehensive Utilization, 1: 70-73.
[4] Chen, X.Y., He, B.Y., Zhang, W. (2018) Research progress in printing and dyeing wastewater treatment. J. Textile Herald, 3: 60-63.
[5] Ministry of Environmental Protection. (2012) GB4287-2012, water pollution discharge standard for textile dyeing and finishing industry. China Environmental Science Press, Beijing.
[6] Yan, D., Feng, Q.Y., Wang, K., et al. (2018) Research status and development trend of advanced treatment technology for printing and dyeing wastewater. J. Modern Salt Chemical, 5: 74-76.
[7] Zeng, X., Zeng, D.F. (2018) Experimental study on deep treatment of printing and dyeing wastewater by Fenton oxidation. J. Guangzhou Chemical Industry, 1: 92-94.
[8] Yao, P., Chen, L., Xu, L., et al. (2018) Process Optimization of Printing and Dyeing Wastewater by
Homogeneous Fenton Process. J. Dyeing & Finishing Technology, 10: 39-42.

[9] Xu, P.Y., Wu, Y., Li, H.Z. (2005) Photocatalytic Degradation of Direct Frozen Yellow Dye by Nano-TiO₂. J. Water Treatment Technology, 12: 31-33.

[10] Wang, G.Y., Han, Y.H., Xu, P.Y., et al. (2017) Photocatalytic degradation of graphene in methylene blue in printing and dyeing wastewater. J. Dyeing and Printing, 22: 40-44.

[11] Suresh, P., Judith Vijaya, J., Balasubramaniam, T. (2016) Synergy effect in the photocatalytic degradation of textile dyeing waste water by using microwave combustion synthesized nickel oxide supported activated carbon. J. Desalination and Water Treatment, 57: 3766-3781.

[12] Concalves, A., Silvestre Albero, J., Serrano Ruiz, J.C., et al. (2012) Highly dispersed ceria on activated carbon for the catalyzed ozonation of organic pollutants. J. Applied Catalysis B-Environmental, 113: 308-317.

[13] Wang, J.L., Bai, Z.Y. (2017) Fe-based catalysts for heterogeneous catalytic ozonation of emerging contaminants in water and wastewater. J. Chemical Engineering Journal, 312: 79-98.

[14] Chen, J., Wen, W.J., Kong, L.J., et al. (2014) Magnetically separable and durable MnFe₂O₄ catalysts for efficient catalytic ozonation of organic pollutants. J. Industrial & Engineering Chemistry Research, 15: 6297-6306.

[15] Moussavi, G., Aghapour, A.A., Yaghaeeian, K. (2014) The degradation and mineralization of catechol using ozonation catalyzed with MgO/GAC composite in a fluidized bed reactor. J. Chemical Engineering Journal, 249: 302-310.

[16] Chen, J., Tian, S.H., Lu, J., et al. (2015) Catalytic performance of MgO with different exposed crystal facets towards the ozonation of 4-chlorophenol. J. Applied Catalysis A-General, 506: 118-125.

[17] Zhao, S., Xu, P.H., Li, G.M., et al. (2017) Study on Ozone Oxidation Flocculation Treatment of Printing and Dyeing Wastewater. J. Journal of Beijing Institute of Petrochemical Technology, 4: 1-5.

[18] Yu, Y. (2018) Design and operation of biochemical effluent from printing and dyeing wastewater in industrial parks with ozone deep treatment. J. Guangdong Chemical Industry, 8: 189-191.

[19] Chen, G.H. (2019) Engineering example of ozone treatment of printing and dyeing wastewater. J. Dyeing and finishing technology, 3: 59-61.

[20] Guan, X.N., Ma, Z.K., Li, Z.P., et al. (2018) Advanced treatment of printing and dyeing wastewater by floating bed ozone catalytic oxidation system. J. Water treatment technology, 11: 80-83.

[21] Zhao, L.H., Nie, F. (2019) Research progress in advanced oxidation technology for water treatment. J. Science and Technology and Engineering, 10: 1-9.

[22] Li, J. (2019) Research progress of advanced oxidation technology in water treatment. J. Environment and Development, 13: 94-95.

[23] Luo, L., Dai, C.Y., Zhang, A.F., et al. (2015) Review of wet catalytic hydrogen peroxide technology. J. Journal of Chemical Industry and Engineering, 19: 3319-3323.

[24] Zhou, S.T., Yang, R.C., Huang, M., et al. (2001) Study on the treatment of high concentration dye wastewater by wet hydrogen peroxide oxidation. J. Chongqing Environmental Science, 2: 62-64.

[25] Lu, T.J. (2010) Experimental study on catalytic wet oxidation (CWOP) treatment of dye wastewater. J. Water treatment technology, 2: 52-57.

[26] He, L., Liu H.Y., Yang, C.P. (2015) Wet-type hydrogen peroxide oxidation reactive brilliant blue KN-R. J. Journal of Environmental Engineering, 9: 4131-4137.

[27] Gu, J.H. (2018) Research and development of printing and dyeing wastewater treatment technology. J. Guangdong Industrial Technology, 13: 27-28.

[28] Wang, Z.Y., Qi, J.Y., Wang, B., et al. (2015) Three-dimensional electrocatalytic treatment of simulated slag wastewater by steel slag particle electrode. J. Journal of Harbin Institute of Technology, 8: 38-42.

[29] Parsaj, B., Merati, Z., Abbasi, M., et al. (2013) Modeling and optimizing of electrochemical oxidation of C.I. reactive orange 7 on the Ti/Sb-SnO₂ as anode via response surface
methodology. J. Journal of Industrial and Engineering Chemistry, 4: 1350-1355.
[30] Irikura, K., Bocchi, N., Romeu, C., et al. (2016) Electro-degradation of the Acid Green 28 dye using Ti/β-PbO₂ and TiPt/β-PbO₂ anodes. J. Journal of Environmental Management, 1: 306-313.
[31] Isarainchavez, E., Baro, M.D., Rossinyol, E., et al. (2017) Comparative electrochemical oxidation of methyl orange azo dye using Ti/Ir-Pb, Ti/Ir-Sn, Ti/RuPb, Ti/Pt-Pd and Ti/RuO₂ anodes. J. Electrochimica Acta, 244: 199-208.
[32] Ye, Z.W. (2018) A/O-Fenton Process for Printing and Dyeing Wastewater. J. Application and Practice of New Technology, 24: 157-158.
[33] Xu, L., Pan, J.J. (2018) Fenton oxidation & Ca(OH)₂ test to study the desorption of biochemical tail water resin in printing and dying wastewater by coagulation combined process. J. China Resources Comprehensive Utilization, 11: 29-32.