The application of electroflocculation (EC) technology in printing and dyeing wastewater

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Abstract. Industrial wastewater contains a large number of toxic pollutants, and the total consumption of dyes in the global textile printing and dyeing industry exceeds 587,000 tons per year. Duo to the process of dye production is more complex, the application of processes and materials are more, so many production links will produce a variety of waste, garbage, and the relevant waste dye into the river, lake and sea is up to millions of kilograms. It can be seen that textile printing and dyeing wastewater is the main source of water environmental pollution. If not treated in time, it will not only affect the production efficiency, but also harm the surrounding ecological environment and pose a serious threat to human survival. Scientific and effective intervention of textile industry wastewater and reasonable selection of textile industry wastewater intervention mode are related to the sustainable development of the industry. In recent years, electroflocculation (EC) technology has gradually become a research hotspot due to its advantages of high removal rate, simple operation, small dosage of chemicals, and small impact on the environment, including the intervention of wastewater. This paper will describe the main mechanism of EC and the application status of EC technology is discussed in detail, the limitations and future development trend of this technology are also proposed.

Keywords: Electroflocculation (EC), wastewater treatment, textile industry.

1. Introduction

In the necessities of human life such as food, clothing, housing and transportation, textiles occupy a pivotal position because of the large demand. As an important traditional industry, textile industry has played a positive role in global economic development, which accounts for 13% to 15% of China's total exports and 5% to 6% of China's total GDP. Although the textile industry may promote the economic development of the country, there are also some downsides, such as the increasing discharge of wastewater. The wastewater mainly contains dirt, grease and various slurries, and dyes added in the processing process. The wastewater is characterized by high concentration of organic matter, complex composition, deep and changeable color, large pH changes, large changes in water quantity and quality, and is difficult to treat. When it penetrates into the underground soil, it may cause soil pollution; Seepage into underground water sources will cause water pollution; Evaporation into the air may also cause air pollution; Moreover, the harmful substances contained may enter the human body through the transmission of the food chain at all levels, thus endangering human health.

According to incomplete statistics, China's printing and dyeing related enterprises discharge more than 4 million tons of wastewater every day, and printing and dyeing wastewater has become an

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important part of the industrial wastewater field. Therefore, the treatment technology of textile wastewater has become a research hotspot in recent years, and how to optimize the treatment scheme is a problem that the current textile printing and dyeing industry must think about and solve [1,2].

The traditional treatment methods mainly include membrane technique, adsorption method, chemical method and biological method. Among them, the membrane technology method and adsorption method are costly, and the chemical method and the biological method need to add chemical agents, which will produce secondary pollution. Electroflocculation (EC) is mainly based on adsorption settlement, supplemented by REDOX, which is the result of the synergistic effect of adsorption, flocculation, REDOX, air flotation separation and other processes. It not only has a condensation precipitation effect on colloids and suspended impurities, but also has a synergistic removal effect on other pollutants in wastewater due to the oxidation of the anode and the reduction of the cathode.

Compared with other water treatment technologies, EC has the advantages of simple operation, non-toxic, no secondary pollution, low carbon, low cost, and may effectively remove COD in wastewater and improve the biodegradability of wastewater. At present, many domestic and foreign researchers have applied EC to catering wastewater, oil wastewater and heavy metal wastewater, etc., but there are few studies on printing and dyeing wastewater treatment [3-5]. This paper summarizes the main application of EC in printing and dyeing wastewater, and puts forward some thoughts and prospects, hoping to provide theoretical reference for the treatment of this type of wastewater.

2. The History of EC

EC technology has a long history, as early as 1887, this process has been used for wastewater treatment. In 1889, London first built electric flocculation treatment of seawater and electrolytic waste liquid workshop. In 1906, The EC technology was first patented in the United States by the German A.E. Deietrich and was used for the treatment of cabin sewage. In 1963, Americans treated municipal sewage by electrochemical coagulation. Due to the low level of early EC technology, high energy consumption and few types of wastewater treatment, it has not been widely used for a long time. In recent years, with the increasing complexity of industrial wastewater types and the increasing demand for small and efficient wastewater treatment integrated equipment, this technology has gradually become a research hotspot, and its research scope covers almost every field of wastewater treatment, including refractory organic wastewater, printing and dyeing wastewater, oilfield wastewater, laboratory wastewater, electroplating wastewater, catering wastewater, smelting wastewater containing heavy metals and other fields [6].

3. The Technical Principle of EC

EC is a water purification method based on electrochemistry, which mainly uses metal aluminum or iron as anode material. Under the action of applied electric field, the metal anode enters the solution in the form of Al³⁺ and Fe²⁺, while the cathode reacts with hydrogen to produce OH⁻. In the solution, Al³⁺ and Fe²⁺ combine with OH to form metal hydroxide floc. Then, the removal of pollutants is realized through the adsorption of floc and pollutant, such as bridge erection and mesh coil.

The EC reaction process is the result of adsorption neutralization, compression flocculation, oxidation and air flotation, and its adsorption capacity is much higher than that of common flocculants [5.7].

The influencing factors of EC include current density, pH, pollutant type and concentration, electrolyte concentration, electrode spacing, etc. The driving force of electrode dissolution, flocculation, and air flotation during the electrocoagulation process comes from the current. Usually, high current density leads to high electrocoagulation efficiency, which in turn increases the amount of metal ion precipitation, generates more flocculants, and enhances the removal rate of pollutants. The rate of cation precipitation satisfies Faraday's law with the applied voltage. Due to the differences in the morphology of different pollutants and metal ion hydrates, there is no unified understanding of the effect of initial pH on pollutant removal. Increasing the electrolyte concentration helps to reduce the energy consumption required for the reaction. The spacing between plates affects the growth and subsequent

flocculation effect of electrocoagulants from a spatiotemporal perspective. The suitable electrode spacing is usually 0.5-2.5cm, and the electrode thickness is 1-2mm. Excessive or insufficient plate spacing is not conducive to improving electrocoagulation efficiency and reducing energy consumption. The higher the initial concentration of pollutants, the greater the reaction time and current density required for EC technology. Extending reaction time can improve the removal efficiency of pollutants, but the removal rate will gradually decrease. Therefore, it is necessary to control reaction time reasonably and reduce the treatment costs.

4. Application of EC

4.1. Sulfide Dyes

The main raw materials for sulfide dyes are aniline, anthraquinone, and phenolic compounds, which have stable and complex molecular structures and are difficult to biodegrade. At the same time, they are insoluble in water, in the dyeing process, it is necessary to add reducing agents such as sodium sulfide and sodium hydrosulfide to reduce it into soluble fiber. Therefore, there may be a large amount of organic compounds and high concentration sulfides remaining in the wastewater of sulfide dyes, making the wastewater extremely difficult to treat.

To solve the problem, six different metals were selected as anodes and graphite as cathodes. The sulfide black dyeing wastewater was treated using EC technology, and the influence of anode materials on EC effect was explored. Orthogonal studies were used to analyze the significance of various factors (applied voltage, flocculation time, initial pH, electrode spacing) on wastewater indicators and the optimal process conditions. It was found that compared to the metal materials such as iron and aluminum, magnesium electrodes have better flocculation effects due to the high activity and larger absolute electrode potential. At a voltage of 15V, the COD removal rate of wastewater reaches 70%, the chromaticity of wastewater is significantly reduced, the sedimentation rate is fast, and the floc structure is stable. The use of magnesium stainless steel electrocoagulation system to treat sulfide black dyeing wastewater has the greatest impact on the COD value and chromaticity of the supernatant due to the spacing between electrodes. The electrolysis time has the greatest impact on the quality of the flocs and the electrode loss rate. The orthogonal experiment showed that when a voltage of 8V was applied, the flocculation time was 20 minutes, the initial pH was 9, and the electrode spacing was 2cm, the comprehensive treatment effect of wastewater was the best. At this time, the COD removal rate was 44%, the chromaticity was 90 times, the electrode loss rate was 12.23%, and the mass of the flocculant reached 1.1246 g [8].

4.2. Dye Wastewater Containing Eriochrome Black T (EBT)

The dye wastewater containing EBT is an essential dye in the dyeing process, which has high chromaticity, complex composition, difficult photolysis and low biodegradation rate, seriously threatens the ecological environment and human health. Dye wastewater simulated by EBT is treated with EC technology. The objective is to observe the effect of different electrolyte and its concentration, current density, initial pH and initial solution concentration on the decolorization rate and chemical oxygen demand (COD) removal rate of dye wastewater. The results show that this technology has good effect on the removal of chroma and COD of dye wastewater. Under the experimental conditions of pure Al plate as electrode, dye wastewater concentration is 100 mg/L, pad spacing is 15 mm, NaCl concentration is 0.75 g/L, current density is 10 mA/cm², and initial pH of solution is 6, with the 20 min electrolysis, the decolorization rate reached 97.5% and the COD removal rate was 61.3%. It shows that the EC process can not only produce flocculates with strong adsorption effect, but also produce strong oxidizing substances that can destroy the chrominance group in the dye molecules, thus reducing the chrominance and COD content of the wastewater [9].

4.3. High Salt Printing and Dyeing Wastewater

High salt printing and dyeing wastewater is one of the industrial wastewater which is difficult to treat. It has the characteristics of high chroma, difficult degradation, high concentration of organic matter, high pH, high salinity and large discharge. The existing research shows that the combination of EC and ozone oxidation technology may improve the decolorization efficiency of printing and dyeing wastewater and save the treatment cost. In one study, the treatment object was simulated printing and dyeing wastewater solution, which was prepared by dissolving reactive dyes and inorganic salts in tap water with reference to actual printing and dyeing wastewater properties. By comparing the cost analysis of simultaneous and step generation of EC and ozone, it is found that under the same conditions, compared with EC→O3 (EC treatment 30 min→O3 treatment 120 min) process, the removal rate of total UV254, COD and TOC increased by 10.16%, 7.18% and 21.41% in EC+O3 treatment for 150 min. The ozone consumed by removing 1mg COD decreased by 0.81mg, and the chroma removal rate of the two was similar. It can be seen that EC+O3 has the higher efficiency [10].

4.4. Flax Fiber Dyeing Wastewater

Flax fiber dyeing wastewater has the characteristics of large changes in water quality, water quantity and water temperature, high organic content, deep color and high pH value. Its pollutants are mainly residual dyes, slurry and additives three organic compounds. In addition, there are more oakum in this wastewater, and the content of lignin, gum and other substances in the wastewater is higher than that of other dyeing and finishing wastewater. Therefore, flax fiber processing wastewater treatment is more difficult. The wastewater coming from dyeing linen was treated through EC. The analysis of EC was done by using a statistical model from where the optimal values for the pH, the current density, and also the treatment time were obtained. EC leads to a maximum reduction of the color (85%), turbidity(65%), and COD(24%) [4].

4.5. Reactive Black KN-B Dve

As a representative of azo dyes, reactive black KN-B has a wide range of applications, so it can be used as a representative dye for the treatment of dye wastewater. One study, based on the technical advantages of electrochemical treatment, explored the treatment of dye wastewater (simulated with reactive black KN-B) by EC and EC-magnetic flocculation. The result showed that EC alone has a certain treatment effect on reactive black KN-B wastewater, remove chroma and COD to a certain extent. Under the best experimental conditions, the decolorization rate of 1000 mg active black KN-B wastewater can reach 95 %, and the removal rate of COD can reach 63%. The combination of magnetic flocculation and EC can obviously enhance the treatment effect of the EC system on the reactive black KN-B wastewater. The combination of magnetic flocculation can increase the decolorization rate by 4 % and the removal rate of COD by 9 % [11].

I.A. Sengil et al. treated the wastewater containing Reactive Black 5 by EC. The electrode spacing was 2.5 cm, the current density was 4.6A/cm2, the amount of sodium chloride was 3 g/L, and the reaction time was 5 min. The chroma removal rate at 591 nm UV is 98.8 %, and the power consumption per kg of dye removal is 4.96 KW·h [12].

4.6. Others

Studies have also shown that electrocoagulation-electroflotation (EC-EF) can show toxicity reduction of textile dyeing wastewater [13]. The results obtained demonstrate the potential of using iron slag as an electrode in the electrocoagulation process in order to reuse industrial waste and reduce costs in the treatment and disposal of solid waste [14].

Aygun et al. used intermittent unipolar parallel EC to treat reactive dye wastewater. The effects of initial pH value, current density and electrolytic time on COD and chroma removal rate were studied by response surface method, and the economic benefits of different electrode materials were compared. Under the optimal reaction conditions, the decolorization rate reached 85.8%, the COD removal rate reached 76.9 %, and the cost of aluminum electrode was 1.84 euros /m3. When the decolorization rate

reaches 92.0 %, the COD removal rate reaches 80.9 %, and the cost of the iron electrode is 1.56 euros /m3. The results show that the cost of iron electrode as sacrificial anode is lower, and it is better than aluminum electrode in COD and chroma removal.

Huijuan Liu et al. adopted a unipolar mode of aluminum plate to treat acid red 14 dye, the current density was 80 A/m^2 , the pH was $6 \sim 9$, and the electrolysis lasted for 4min. The removal rates of COD and chroma are 85 % and 95 %, respectively. The study also proves that the removal rate of chroma in unipolar mode is higher than that in bipolar mode. However, the reason is not clear and needs further study.

5. Limitation

Although the EC method has many advantages, it also has some shortcomings: (1) the conductivity requirement is relatively high, and the conductivity corresponds to the conductive characteristics of the water body, which can directly affect the removal efficiency of pollutants and the operation energy consumption; (2) Metal ions are produced after anode metal electrolysis, which spontaneously hydrolyzes to form hydroxide flocculation precipitation, but some flocculation is often left after the treatment of pollutants; (3) The surface of the metal anode will be passivated, causing the metal oxidation rate to slow down, the current efficiency to reduce and the operating power consumption to increase. The commonly used methods to eliminate electrode passivation include mechanical removal, electrochemical cleaning and reverse pole method [15,16].

6. Conclusion

Electroflocculation(EC) is a complex physicochemical reaction process. As an environment-friendly technology, it has a wide application prospect in textile wastewater by virtue of its unique advantages. However, there are still many problems in the current research status, such as the effect of EC treatment is affected by complex factors, and it is difficult to control the reaction conditions comprehensively. Electrode passivation and polarization are common in the water treatment process, which reduces the removal effect of EC and increases the energy consumption. At the same time, the effect of comprehensive application of different technologies depends on the specific wastewater water quality characteristics and treatment requirements, the future research of textile industry wastewater treatment technology will tend to be intelligent and automated.

With the continuous development of science and technology, intelligent sensors, automatic control systems, big data analysis and other technologies will be widely used in wastewater treatment, to achieve real-time monitoring of the wastewater treatment process, optimize control and automatic operation, and then improve the treatment effect, reduce human error, while reducing operating costs to a certain extent. The research should also conduct in-depth research on the mechanism of various treatment methods in the wastewater treatment process from the micro level to the macro level, reveal the complex mechanism of wastewater treatment, and provide scientific theoretical basis for optimizing the treatment process and improving the treatment effect.

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