

In the Anodizing Dyeing Process of Aluminum Alloy Chemical Oxidation Method for Organic Dye Wastewater Treatment

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Abstract

Aluminum is the most widely used and widely used metal material in non-ferrous metals. Aluminum and aluminum alloy products are widely used in our daily life because of their superior performance. For corrosion resistance and aesthetics, we will anodize the aluminum surface and its alloys. It makes the aluminum products have a colorful appearance, meets the aesthetic needs of people in modern society, and more effectively exerts the functions and use effects of the products. But in the dyeing process, colored wastewater is produced. This paper mainly focuses on how to treat organic dyes (colored) quickly and at low cost in the process of wastewater treatment, so as to achieve the process of qualified discharge.

Keywords

Anodizing of aluminum alloy; Organic dyes; Chemical oxidation; Sodium hypochlorite

Introduction

Under the premise of increasingly stringent national environmental protection policies, every company must undergo strict standardized treatment of waste gas and wastewater generated during the production process in order to meet national emission standards before it can be discharged, as shown in Table 1.

Table 1. Emission Limits for the Pearl River Delta Region (Electroplating Wastewater Pollutant Discharge Standard, DB44/1597-2015)

project	COD _{cr}	SS	NH ₃ ·N	TN	Total phosphorus	P H
unit	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	Dimensionless
Upper limit value	80	30	15	20	1	6-9

Aluminum is an amphoteric metal, reacting chemically in both acidic and alkaline media. Its alloys are also unstable, exhibiting not only general corrosion in a few media but also pitting corrosion, galvanic corrosion, crevice corrosion, intergranular corrosion, filiform corrosion, and lamellar corrosion. To overcome these drawbacks and improve its protective, decorative, and functional properties, anodizing is the most common protective method. Aluminum anodizing is an electrolytic process where the surface of aluminum or aluminum alloys is transformed into a porous

oxide film in an electrolyte (limited amounts of sulfuric acid, oxalic acid, chromic acid, phosphoric acid, or sulfuric acid with organic acids; sulfuric acid is commonly used). This film provides protection, decoration, and functionality.

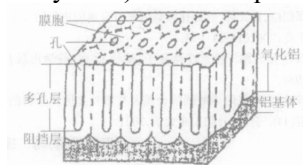


Figure 1. Structure of anodic oxide film.

The thickness of porous anodic oxide films ranges from a few micrometers to tens of micrometers, with pore sizes of approximately 0.01~0.03 μm and a pore count of approximately 10^{10} pores / cm^2 . The oxide film exhibits strong adsorption properties. To enhance decorative appeal, a coloring process is often performed after anodizing. Various coloring methods exist, including natural coloring, electrolytic coloring, organic coating coloring, composite coloring, and adsorption coloring. Utilizing the adsorption properties of the oxide film, adsorption coloring is frequently used in the anodizing and dyeing process of aluminum alloy surfaces. This allows the aluminum surface to be dyed in various colors, improving its decorative properties and creating a colorful aluminum world. This article mainly introduces the use of the oxide film's characteristics to apply organic dyes, resulting in various colors on the aluminum surface. This production process generates colored wastewater characterized by large volume, high color intensity, complex composition, and a wide range of water quality variations.

Organic dyes are organic compounds containing a color-producing group—the chromophore. These groups are all unsaturated groups, such as: $>C=C<$, $>C=O$, $>S=O$, $-\text{CH}=\text{CH}-$, $-\text{CH}=\text{N}-$, $-\text{N}=\text{N}-$, $-\text{N}=\text{O}-$, etc. These chromophores are attached to hydrocarbons with special structures (such as aromatic hydrocarbons) to form the chromophore of the compound.

Dye wastewater is characterized by its deep color, high COD concentration and organic pollutant content, complex composition, high levels of heavy metals and biotoxicity, and difficulty in biodegradation. Dyes themselves exhibit strong resistance to photolysis and oxidation, and contain various organic compounds with biotoxicity or "three-way" (carcinogenic, teratogenic, and mutagenic) properties, posing a significant threat to environmental pollution. Its main hazards are as follows:

(1) Color pollution of dye wastewater to the environment: Dyes in wastewater can absorb light, reduce the transparency of water, consume a lot of oxygen in the water, cause water hypoxia, affect the growth of aquatic organisms and microorganisms, destroy the self-purification of water, and easily cause visual pollution.

(2) Pollution of the environment by the toxicity of dye wastewater: Dyes are aromatic halides, aromatic nitro compounds, aromatic amines, biphenyls and other polycyclic aromatic compounds formed after the hydrogen on the benzene ring of organic aromatic compounds is replaced by halogens, nitro groups and amino groups. They are all highly toxic to organisms, and some are even carcinogenic, mutagenic and teratogenic substances.

(3) Pollution of the environment by heavy metals in dye wastewater: Heavy metals present in dyes, such as chromium, lead, mercury, arsenic, zinc and other heavy metal salts in wastewater, cannot be biodegraded. They can exist in the natural environment for a long time and will be continuously transferred through the food chain and accumulate in the human body.

(4) Dye wastewater has a high organic content, complex composition, and high content of harmful substances, which leads to eutrophication of water bodies after discharge. If dye wastewater is not properly treated before discharge, it will pose a great threat to the increasingly scarce drinking water source. Therefore, wastewater treatment can not only reduce or avoid environmental pollution and protect people's health, but also recycle the treated water and save water resources.

1. Common problems exist in the treatment of dyeing wastewater

1.1 Treating dyeing wastewater requires capital investment

1.2 Insufficient attention was paid to this issue; after resolving the color issue, standards for other emissions were not considered

1.3 Inadequate processing technology and lack of testing equipment

To address the environmental pollution caused by organic dyes, various methods and technologies have been

employed to treat dye wastewater, with the main objectives being:

(1) Separate and remove the enriched chromogenic substances;

(2) It destroys the chromogenic substances to achieve decolorization and degradation of organic matter. Methods for treating dye wastewater include physical adsorption, chemical (chemical reduction) treatment, and biological treatment (through subsequent expansion of the treatment process, adding anaerobic and aerobic tanks). However, from a cost perspective, physical adsorption and flocculation methods increase investment costs (due to significant losses in site and treatment agents). Using chemical oxidation methods, commonly used chemical methods in dye wastewater treatment include flocculation sedimentation, chemical oxidation, electrochemical methods, and photochemical oxidation. Chlorination oxidation is currently a relatively mature method for decolorizing dyeing and printing wastewater. It utilizes various oxidants to break the unsaturated bonds of the chromophores in dye molecules, forming smaller organic or inorganic compounds, thus causing the dye to lose its color-producing ability. Commonly used oxidants include ozone and chlorine. Chemical oxidation, on the other hand, uses oxidation to destroy the conjugated system or chromophores of the dye, and is a method for decolorizing dyeing and printing wastewater, and one of the main methods for decolorizing and degrading dye wastewater. Oxidants such as polyaluminum chloride, polyacrylamide, and sodium chlorate have extremely strong destructive capabilities and can rapidly react with organic matter in wastewater, thereby reducing COD. Strong chlorine-containing oxidants and inorganic polymers react with ammonia nitrogen in wastewater, thereby achieving the purpose of removing ammonia nitrogen from the wastewater. It can significantly degrade the concentration of ammonia nitrogen in wastewater, and simultaneously utilizes its properties to inorganicize organic pollutants in the wastewater during the reaction process, effectively reducing the content of organic pollutants. It can be used alone or in combination with commonly used inorganic and organic flocculants or coagulants. This article mainly introduces how to use chlorination oxidation to quickly and cost-effectively decolorize and remove COD and ammonia nitrogen, followed by flocculation and subsequent treatment to achieve emission standards. Practical verification has shown that this method has achieved good results.

2. Experimental Materials

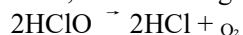
- (1) 84 disinfectant (chlorine content 5%)
- (2) Primary sodium hypochlorite solution. (Chlorine content 12%)
- (3) Secondary sodium hypochlorite solution (chlorine content 10%)
- (4) Bleaching powder. (A mixture of calcium hydroxide, calcium chloride, and calcium hypochlorite, with calcium hypochlorite $[\text{Ca}(\text{ClO})_2]$ as its main component and an available chlorine content of 30%-38%).
- (5) Decolorizing agent and activated carbon.
- (6) Dye mixing wastewater. (Wastewater from the centralized equalization tank in production)
- (7) Black dye wastewater.
- (8) Colored wastewater after passing through the wastewater treatment system
- (9) Flocculants (polyaluminum chloride, polyacrylamide)

3. Experimental Principle

Organic dye molecules generally contain chromophores, such as azo groups ($-\text{N}=\text{N}-$), carbonyl groups ($>\text{C}=\text{O}$), and quinone structures. Adding sodium hypochlorite can break the unsaturated bonds in the molecular structure, causing the dye molecules to oxidize and decompose, generating organic acids, aldehydes, and other substances with smaller molecular weights, thereby losing their color.

The bleaching principle is as follows:

$\text{ClO}^- + \text{H}_2\text{O} = \text{HClO} + \text{OH}^-$ occurs when hypochlorite ions hydrolyze to produce hypochlorous acid. Hypochlorous acid then decomposes to produce nascent oxygen, which has strong oxidizing properties. This strong oxidizing agent reacts with organic dyes. This reaction is irreversible, thus reducing color intensity and achieving a bleaching effect.



4. Experimental Procedure

Black dye wastewater from different treatment processes was collected, and different treatment chemicals were added to compare the treatment effects.

- (1) Black dye wastewater (1000ml)
- (2) Dye-mixed wastewater (1000ml)
- (3) Colored wastewater after passing through the wastewater treatment system

(1) Using (1), we added different treatment agents and observed the results, as shown in Table 2.

(2) Wastewater from different treatment processes (1), (2) and (3) is used, and secondary sodium hypochlorite solution is added simultaneously, as shown in Table 3.

For the above three types of wastewater, adding secondary sodium hypochlorite directly to the dyeing wastewater at a concentration of 5‰ can achieve effective decolorization. However, pre-treating the dyeing wastewater at this stage is the most cost-effective approach.

5. Dyeing wastewater treatment process

The dyeing wastewater treatment process is shown in Figure 1.

After decolorization, the wastewater's pH is adjusted with sodium hydroxide. Then, through the combined action of polyaluminum chloride and polyacrylamide flocculation, the oil in the water is separated. After skimming off the floating oil and scum, the clear liquid flows by gravity into the primary sedimentation tank. Once in the primary sedimentation tank (the original tank), the water comes into contact with flocculants again. The suspended solids in the water are adsorbed by the flocs formed after the flocculants dissolve. Due to the difference in specific gravity between the flocs and the water, the flocs gradually settle. After compression and sedimentation, the flocs form a compact physicochemical sludge layer at the bottom of the beaker, ultimately completing the initial solid-liquid separation. The water that has undergone solid-liquid separation is then filtered, and the data are analyzed (see Table 4).

After decolorization and operation according to the process flow, the test data is shown in Table 5 below. The emission standards are met.

Table 2

Duration of stay Treatment solution	10 minutes	1 hour	2 hours	4 hours
84 disinfectant (5ml)	Slight discoloration	Slight discoloration	Slight discoloration	Slight discoloration
Sodium hypochlorite solution (5ml)	Decolorized to red	The color changed to reddish-yellow.	The color changed to reddish-yellow.	The color fades to a light yellow.
Secondary sodium hypochlorite solution (5ml)	Decolorized to red	The color fades to a light red.	The color changed to reddish-yellow.	The color fades to a light yellow.
Bleaching powder (5g)	Slight discoloration, cloudy	Slight discoloration, cloudy	Slight discoloration	Slight discoloration, cloudy, not much change
Decolorizing agent and activated charcoal (5ml/appropriate amount)	Unbleached	Unbleached	Slight discoloration	The color saturation is also quite high.

Table 3

Duration of stay Wastewater treatment	10 minutes	1 hour	2 hours	4 hours
Black dye wastewater (1000ml)	Decolorized to red	The color fades to a light red.	The color changed to reddish-yellow.	The color fades to a light yellow.
Dye-mixed wastewater (1000ml)	Decolorized to red	The color fades to a light red.	The color changed to reddish-yellow.	The color fades to a light yellow.
Colored wastewater after passing through the wastewater treatment system	The color fades to a light red.	The color fades to a light yellow.	The color fades to a light yellow.	The color fades to a light yellow.

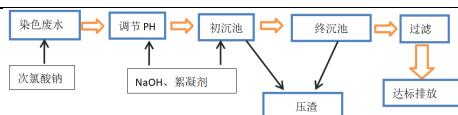


Figure 1. Process Flow Diagram.

Table 4. Raw water test values

project	COD _{cr}	TN	color	P H
unit	(mg/L)	(mg/L)	Dimensionless	Dimensionless
numerical values	114.4	81.46	Reddish	5.5

Table 5. Test values of treated water

project	COD _{cr}	TN	color	P H
unit	(mg/L)	(mg/L)	Dimensionless	Dimensionless
numerical values	18.06	5.908	colorless	8.36

6. Conclusions

Secondary sodium hypochlorite solution (containing 10% chlorine) can treat wastewater and is economical.

Treatment process: Dyeing wastewater → secondary sodium hypochlorite water (chlorine content 10%) (to reduce color) → pH adjustment → flocculant addition → sedimentation → filtration (sand filter can be used) → to meet discharge standards.

In conclusion, the lowest-cost process and chemical oxidation method can be used to solve the problem of dyeing wastewater.

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