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The impact of different types of wastewaters on electrode passivation in electrical coagulation systems

Jie Ying[1,4,5,†], **Yingru Yuan**[2,6,†], **Shiran Xin**[3,7,†]

[1]University of Nottingham Ningbo China, Ningbo, 315199, China
[2]Dipont Huayao Collegiate School Kunshan, Kunshan, 215301, China
[3]Hongwen School Qingdao Campus, Qingdao, China
[4]Corresponding author

[5]sgyjy2@nottingham.edu.cn
[6]Yingru_yuan@163.com
[7]claudia@boardest.net
[†]All the authors contributed equally to this work and should be considered as co-first author.

Abstract. Water is a crucial part of the production process when the company uses reaction or cooling water to create customized goods. It is therefore expected that some of the chemical components from the boats will be present in the water. Ensuring the safety of discharged water into rivers for human consumption is vital, as water supplies are limited and subject to cycles. Industrial wastewater sometimes includes higher concentrations of heavy metals like copper, lead, and other pollutants, whereas domestic wastewater usually has higher amounts of nitrogen and phosphate. Our previous strategy to dealing with these components involved adding chemicals and filtering them, but this method introduced additional compounds into the water sample. Science and technology have advanced alongside sewage treatment techniques. In this paper, we investigated the effects of electrical coagulation on water treatment in a rapidly industrializing environment. The effectiveness of electrical coagulation has been extensively studied, but less is known about how it impacts aquatic habitats and machinery. This work addresses the issue of equipment passivation in a number of potential methods that are related to an improvement in water quality.

Keywords: Water treatment, Industrial wastewater, Domestic wastewater, Electrical coagulation, Machinery and equipment passivation

1. Introduction

In recent years, EC (Electrocoagulation) technology has been used in an increasing number of novel water treatment systems. Hence, the theory of employing EC in wastewater treatment was initially proposed by a British scholar named P. P. STROKACH. After the 1950s, America and the former Soviet Union had already done tons of research on wastewater about the EC and used it in river water, municipal wastewater, and chromate wastewater. At the beginning of the 21st century, the rapid development and large-scale use of chemical flocculants, as well as the underdevelopment power industry, led to the slow development of EC. Nowadays, EC has become the research hotspot of water treatment technology. It had a huge impact on the economy by decreasing waste and increasing the possibility of reusing [1].

Electrical coagulation will also produce some insoluble materials at the same time, which will stick to the surface and stop the process from moving forward [2]. Consequently, the influence of electrode passivation and various techniques to slow down passivation will be the main topics of this study.

2. Function of Electrical Coagulation and Passivation process

An electrolytic cell is an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction. It has two electrodes and can conduct electricity. One electrode loses electrons, the valence state of the element becomes high, and the oxidation reaction occurs; the other electrode gets electrons, the valence state of the element becomes low, and the reduction reaction occurs. An example of electrolytic cells can be shown in Figure 1.

Electrode passivation is when an insulating layer develops on an electrode's surface, obstructing the flow of ions and electrons necessary for the electrochemical reaction. As reaction byproducts, impurities, or solid deposits build up over time, they may form a passivation layer. Electrochemical processes that reduce the electrode's active surface area can also lead to passivation by forming oxide or hydroxide layers or by causing passivation.

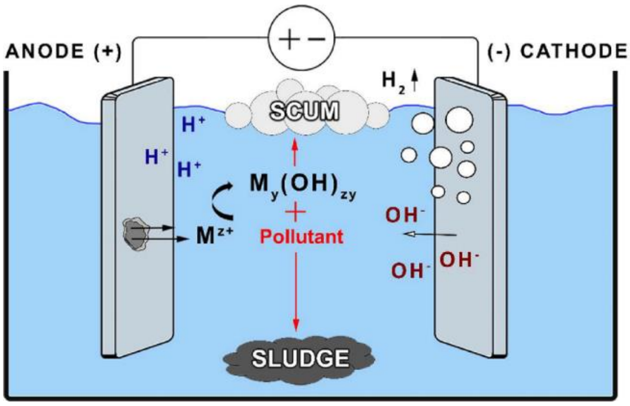

Figure 1. A demonstration of the principle of electrocoagulation

Usually, electrical coagulation uses aluminum or iron for the anodes. For aluminum anodes, the aluminum strip will lose electrons, forming aluminum ions. At the same time, H2(g) and OH-(aq) are produced when H2O (l) is electrolyzed at the negatively charged cathode [3]. Thus, Al3+ will react with OH- and form Al (OH)3. The electrode-electrolyte interface's passivation layer impedes kinetics and raises resistance there [4]. The aluminum strip dissolves in this process, forming a flocculent precipitation of aluminum hydroxide. Aluminum hydroxide is a kind of colloidal pollutant. The negative surface charge of colloidal pollutants will be neutralized by metal cations dissolved in the water, causing a bigger aggregate to form that can be filtered [2]. The goal of eliminating hazardous substances from the solution can be accomplished by precipitation, which can cause some soluble ions to be adsorbed away. The functions can be written below as Equation 1, Equation 2, Equation 3 and Equation 4.

$$Al - 3e^- = Al^{3+} \tag{1}$$

$$Al^{3+} + 3H_2O = Al\ (OH)_3 + 3H^+ \tag{2}$$

$$H_2O(l) = H^+(g) + OH^-(aq) \tag{3}$$

$$2H^+ = H_2\ (g) \tag{4}$$

Most of the aluminum hydroxide can form a precipitation which can be removed, but at the same time, a small portion of the flocculent precipitation will combine with the electrode contact, coating the electrode's exterior and stopping the reaction. This process is known as passivation of the electrode. Polarization studies can be used to describe the characteristics of electrode passivation [2].

In comparison for the iron anode, it works the same process but produces different precipitated products, such as Fe (OH)2 or Fe (OH)3. The final product of the reaction is related to the ionic properties in the solution, and the difference in the product will also affect its passivity, which will be discussed later in section 4.

3. Effect of ion types on electrode passivation

3.1. Industrial wastewater

3.1.1. Wastewater with chloride ions. Using the manufacture of iron as an example, hydrochloric acid is required to eliminate the oxide that will be present on the surface of the metal. Thus, the chloride ions will be represented in the wastewater. Pitting often happens in this kind of solution. The electrode surface layer is broken down by aggressive ions, such as Cl-, or the surface film dissolves when the electrode boundary layer gets sufficiently acidic due to metal hydrolysis [2]. Cl- has a high ionic mobility and can therefore pierce the oxide coating covering the electrode surface [2]. Therefore, when Cl- combines with the metal oxides, the surface layer dissolves, and the underlying raw metal is exposed [5]. In other words, electrode passivation won't cause as much interference with the electrodes in this solution.

The penetration of chloride ions is, however, constrained, and more precisely, the pore size and gap on the surface of the oxide film generated by aluminum hydroxide or iron hydroxide are different. Although the precise mechanism of action will not be covered in detail in this article, it is obvious that the type of ions present in the solution affects the degree of passivation of the electrode.

3.1.2. Wastewater with fluoride ions. The fluoride ions can have favorable or unfavorable effects on the water quality which depends on the concentration of this kind of ion. High concentrations of fluoride ions may cause different diseases at different ages [6].

As the fluoride ions have a high level of corrosiveness the electrodes in electrocoagulation are made of metals like iron (Fe) or aluminum, which can be corrosive heavily [7]. The electrodes may have a passive film on the surface to prevent the ions that have strong causticity from damaging electrons from working as usual. HF, on the other hand, can "accelerate the transfer of oxides into fluorides on the iron surface, which is the most common material as an electrode to damage passive film in 1M HClO4 solution containing 0.1 M HF," as it is another type of component found in wastewater. Furthermore, because fluoride ions have the highest electronegativity (4.0) of any halide element, they have a stronger affinity than chloride ions to attract other types of molecules and ions that polarize other substances and aggravate their solution in a mixed solution, which is similar to the conditions found in wastewater treatment factories. That is the reason why fluoride ions have such a strong corrosiveness, and the passivation happens during the EC process.

3.1.3. Wastewater with heavy metals. The main types of heavy metals in industrial wastewater are chromium, cadmium, lead, copper, zinc, and nickel. Most of the materials come from places such as the iron, steel, and petrochemical industries [8].

The metals in the wastewater will affect the electrodes in several ways:

1. Scaling: Heavier substances will gather on the surface of the electrode, causing scaling. The performance of the electrode is negatively affected by this dirt, which also reduces conductivity and increases resistance [9].
2. Corrosion: When the electrode is exposed to certain heavy metals in wastewater, such as lead or copper, the electrode will corrode. Over time, this corrosion weakens the electrode material, leading to shorter life and lower effective operation [1].

3. Interference with electrochemical reactions: Heavy substances may also hinder the electrochemical reactions that occur on the electrode surface. For example, some metals in wastewater may act as catalysts for unwanted side reactions, which may reduce the overall effectiveness of the electrode system [10].

3.2. Domestic wastewater

3.2.1. The organic materials in domestic sewage. There are several organic materials in domestic sewage. BOD can measure the biomass inside solution by comparing the oxygen consumption; there are also other elements in the domestic sewage are nitrogen, phosphorus, and ammonium.

For proteins, electrode scaling can occur when proteins are absorbed to the electrode surface by electrostatic or hydrophobic contact. The electrode’s effective surface area will decrease due to protein scaling, which will also impede the electrochemical reaction at the electrode interface. Protein fouling on electrodes has been the subject of several research [11].

The BODs (Biochemical oxygen demand) value can reflect the amount of organic matter in the water, especially the microorganisms. If the BOD is high, the water condition is suitable for microorganisms to survive and reproduce. It will cause problems: One is that when the BOD value is very high, organic compounds will oxidize the anode to survive, and in this process by-products, such as organic acid, will be produced. Acidity accelerates the passivation process of the electrode. In addition, when the BOD value is very high, the oxidation of organic matter will cause the formation of a passivation film on the electrode surface. These membranes are often composed of organic compounds or metal oxides, which hinder electrochemical reactions and reduce the overall efficiency of the coagulation process. These biofilms can act as an insulating layer, inhibiting electrochemical reactions and promoting electrode passivation.

Nitrogen takes the largest percentage as a component in air, so nitrogen comes into and dissolves in water to form ammonium as the product. These two components may stimulate the growth of bacteria in the wastewater to convert nitrogen and ammonium into nitrate ions, which may corrode the electrodes through adsorption mechanisms, mostly as “competitive absorption” against chloride on the metal surface. Since the nitrate ions may have similar access to absorb on or enter into a local site on the metal surface. More bacteria are promoted to grow consequently, the efficiency of electrocoagulation decreases and the subsequent processing of the bacteria to achieve high-quality water is more difficult.

3.2.2. Pathogenic microorganisms. For metalloprotein structures to be stabilized and to perform to their maximum potential, pathogenic bacteria need metal ions as nutrition [12].

That is, the solution containing microbial pathogens will utilize more electrodes if the entire number of waste ions in the solution is known, resulting in less precipitation overall. Consequently, the material might be lowered by the electrode under the same circumstances, which lowers the effectiveness of electric flocculation.

Additionally, as many pathogenic bacteria are resistant to sterilizing by ultraviolet light, acid and alkali, and high temperatures, these wastewaters carrying a lot of pathogenic germs will harm human health. Figure 1 shows the basic structure of a virus.

Then, as bacteria in this act as solid suspended matter, the water body becomes murkier, decreasing the effectiveness of electrolysis.

In a word, pathogenic microorganisms can reduce the efficiency of electrical coagulation.

4. Effects of electrode passivation

4.1. The quality of water

The smell of water will be changed in two aspects.

1. Organic matter accumulation

When electron scaling happens, the organic substances cannot be composed completely and these components will accumulate at the water bottom, like methane, and sulfuretted hydrogen.

2. Anaerobic condition

Excessive amounts of nitrogen and phosphorus can cause anaerobic conditions which can promote the anaerobic reaction that occurs between some left organic components to form sulfuretted hydrogen, methane, or carbon dioxide which have a foul smell.

4.2. Treatment efficiency and cost

The common methods for treating electrode passivation are Electrochemical Activation, Chemical Treatments, and Mechanical Treatments. When facing the passivation problem, the operator should choose a specific method based on the real situation, but all of them are efficient for solving the problem and make the electrode back to normal and healthy state.

The electrochemical activation method involves providing an electric potential to the electrode, which helps to remove the passivation layer through an electrochemical process. Anode polarization is a popular technique that involves exposing an electrode to a positive voltage to oxidize a passivated substance. The method can improve the electroactivity of the electrode while recovering the surface of the electrode [13].

For chemical treatment, it has multiple processes for removing the passivation layer. The characteristics of the electrode material and passivation layer will determine which acid is best. The passivation layer will disintegrate or corrode when pickling with a powerful acid like sulfuric or hydrochloric acid. When removing metal oxides or hydroxide passivation layers, for instance, hydrochloric acid (HCl) or sulfuric acid (H2SO4) might be utilized. To prevent excessive etching or harm to the electrode surface, the concentration and length of acid exposure should be carefully managed. Based on the passivation material's makeup, it may be treated with alkaline solutions or organic solvents [14].

Mechanical treatments are physical methods that remove the membranes directly. One of the mechanical treatments is brushing or scrubbing. This includes manually or mechanically cleaning the electrode surface with a brush or abrasive pad that is resistant to chemicals. The new electrode material is made visible by mechanical stirring, which also aids in removing the passivation layer. To prevent causing the electrodes severe harm, brushing or cleaning should be done with caution. By physically removing the layer, the underlying active electrode surface is made visible. However, during this procedure, care should be taken to prevent injuring the electrode [15].

The cost of electrode passivation treatment may depend on a few variables, including the treatment technique selected, the magnitude of the treatment, and the accessibility of the necessary resources and equipment.

1. Electrochemical activation: The expense of electrochemical activation therapy depends on the particular facilities and equipment needed. In this method, specialized electrochemical cells or reactors, power systems, and control systems may be used. Investment in equipment, upkeep, and electricity usage are all costs. The price of any chemicals or solutions employed in the process should also be taken into account. It is challenging to offer a precise cost estimate without more details regarding the size and complexity of the activation configuration.

2. Chemical treatment: The price of chemical treatment for electrode passivation depends on the kind and strength of chemicals employed, the volume and frequency of treatment, as well as the treatment. The cost of chemicals, the removal of waste liquids, and any essential safety precautions are just a few examples. The cost of chemical treatment is generally thought to be lower than that of other techniques, although the precise chemical employed, and the scope of the treatment will affect the final price.

3. Mechanical treatment: To remove or lessen the passivation layer on the electrode surface, mechanical treatment uses physical methods like polishing or wear. The expense of mechanical treatment may vary depending on the tools needed (such as polishers, wear tools, and other tools), the

manpower needed, and the intricacy of the passivation layer. The price will change according to the size, quantity, and frequency of the treated electrodes [16].

Overall, treating electrode passivation is complicated, and the cost varies. The treatments can also be added together to treat a specific situation. Therefore, people cannot judge the efficiency of the method based on the cost.

5. Solutions to the problem of electrode passivation (methods) & modern technological developments

Based on the functions of electrode passivation, several modern techniques can be used in electrochemical activation systems to lessen electrode passivation.

Cleaning the electrodes frequently is one way to address electrode passivation. Cleaning the electrode aids in removing the accumulated dirt and active chemicals that might cause passivation. For this purpose, physical brushing and ultrasonic cleaning are frequently employed methods [17][18]. By periodically cleaning the electrodes, the passivation layer may be decreased, consequently enhancing electrochemical performance.

Another technique to tackle electrode passivation is to change the electrode surface. Electrodes' performance can be enhanced, and passivation can be decreased by coating them with catalytic compounds or protective coatings [19]. For instance, investigated the use of TiO2 and WO3 thin films on graphite electrodes.

6. Conclusions

Electrode passivation is a typical occurrence, and the level of passivation is influenced by the solution's characteristics and the kind of electrode plate. The likelihood of ions forming surface scale increases with the amount of adsorbent ions present, necessitating routine cleaning or electrode replacement.

There are now three major ways to clean a motor, each with their own benefits. The chemical cleaning approach is the one that is most frequently employed because it is thought to be the least expensive.

There are two approaches to dealing with the issue of electrode passivation: one is to regularly clean the electrode, and the other is to coat the electrode's surface.

Overall, it is challenging to avoid electrode passivation since the level of passivation varies according on the kind of wastewater. Therefore, although routine cleaning of the electrode can slow down the passivation process, regular electrode replacement is still necessary.

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All the authors contributed equally to this work and should be considered as co-first author.

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