Study on Electrocatalytic Oxidation Technology of Domestic Sewage

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Abstract. Domestic sewage is treated by graphene-based electrocatalytic oxidation process when adding salt or not. The results show that the removal rate of ammonia nitrogen and COD are 97.86% and 64.29% separately under the conditions of 1g/L salt, 4min residence time and 500A/m² current density. The COD and ammonia nitrogen of produced water are 72.5mg/L and 1.35mg/L respectively which meet the comprehensive wastewater discharge standard of GB8978–1996, while the removal rate of ammonia nitrogen and COD are 97.22% and 74.55% separately under the conditions of 20 min residence time and 190A/m² highest current density without adding any salt. The COD and ammonia nitrogen of production water are 57mg/L and 1.7mg/L respectively which meet the comprehensive wastewater discharge standard of GB8978–1996 too. In the experiment, about 95.11 % ~ 97.27 % of ammonia nitrogen is converted into nitrogen. The cleaning effects of the deposition by using hydrochloric acid and citric acid are investigated. The results show that the deposition can be cleaned by both of the 2% hydrochloric acid and 2% citric acid, but the immersion cleaning rate of citric acid which has residual left is slower than hydrochloric acid. The deposition can be thoroughly cleaned by cycle operation.

1.Introduction
In recent years, Domestic sewage treatment in rural areas has received great attention as an important task of rural revitalization strategy and the risk of excessive discharge of domestic sewage has gradually increased. The treatment of domestic sewage [1-2] is mainly carried out in sewage treatment plants. However, some areas are restricted by geographical and natural conditions, such as remote areas and rural areas, where the domestic sewage output is small, the production area is scattered, the composition is complex, and the water quality fluctuates greatly. The centralized treatment is difficult. If all the sewage is collected in a sewage treatment plant for centralized treatment, it will spend a lot of infrastructure costs, operation costs, maintenance costs and serious waste of equipment resources. The conventional treatment methods are mainly septic tank, traditional biochemical method and buried domestic sewage treatment devices. The dispersed small flow domestic sewage has the problems of less discharge and discontinuity, while the power sewage treatment devices need to adjust the water level in the pool to reach the minimum treatment capacity before operating the equipment, otherwise the start frequency of aeration blower and submersible pump is too low.

On the other hand, power sewage treatment devices have large technical problems in practical projects. The mud production is large and there are few professional maintenance staff there.
Submersible sewage pumps, blowers, control systems, and power sources of sewage treatment devices appear different degrees of failure which affect the continuous operation of the equipment and the effect of sewage treatment.

Traditional technology has problems such as large area, poor operation effect, and substandard water production in the decentralized small-flow domestic sewage treatment. Therefore, it is of great significance to study more economical, efficient, and universally adaptable electrocatalytic oxidation technology. This technology has great advantages in treating the above-mentioned domestic sewage.

The use of electrocatalytic oxidation technology to treat domestic sewage is a hot spot in recent years. The electrocatalytic oxidation technology for domestic sewage treatment has the advantages of no need to add oxidants, flocculants or other chemicals. Meanwhile, The equipment is simple and small which need less space and its operation is flexible, especially it has the most practical significance in the areas with high environmental quality requirements, small amount of water treatment, and remote areas. This method is suitable for the treatment of general domestic sewage, but the electrocatalytic oxidation technology has the disadvantages of high power consumption, high cost, oxygen evolution and hydrogen evolution side reactions problems. In recent years, the continuous progress of electrocatalytic oxidation technology and the application of new electrode materials have provided newer and more effective solutions for the treatment of sewage by electrochemical methods. The purpose of this study is to select appropriate operating parameters and observe the treatment effect of COD, ammonia nitrogen and total nitrogen in domestic sewage.

2. Materials and Methods

2.1. Electrocatalytic Oxidation Technology

Electrocatalytic oxidation technology is upgraded on the basis of electrochemical reactions, using metal oxide materials with good catalytic performance as the anode which generate active free radicals with strong oxidation performance to oxidize and degrade organic matter. The generated active group was used for the oxidation-reduction reaction of organic matter in wastewater to degrade them into small molecular organic matter or completely oxidize them into CO₂ and water, so as to achieve the purpose of wastewater treatment.

This technology can be divided into direct oxidation on and near the anode surface and indirect oxidation away from the electrode surface, which has attracted widespread attention in the field of water treatment.

Direct oxidation is to directly oxidize the pollutants into smaller substances on the surface of the anode in an external electric field to achieve the purpose of removing pollutants.

Indirect oxidation is under the action of an external electric field, using the strong oxidizing intermediate produced by electrolysis as an oxidant. The pollutants are converted into less toxic products or completely mineralized. This process is irreversible. The produced oxidants are such as Chlorine, hypochlorite and peroxide.

Electrocatalytic oxidation technology has the following characteristics.

1) High compatibility with the environment. The removal of pollutants by electrocatalytic oxidation technology mainly depends on electrons, without adding chemicals, avoiding secondary pollution caused by chemicals, and almost no selectivity to organic oxidation.

2) The equipment is simple, covers a small area, equipment maintenance is easy.

3) The reaction conditions are mild, not affected by the climate, suitable for use in any region

4) The equipment is simple and the floor space is small. It is easy to realize automatic operation. The reaction is highly controllable

2.2. Graphene Electrode

Graphene is a two-dimensional (2-D) carbon atom sheet connected by SP² hybridization. This structure determines graphene has special properties. For example, the surface area is very large. Theoretically, the surface area of single-layer graphene is 2630 m²/g, which is twice that of single-
walled carbon nanotubes. Thermal performance \((k=5 \times 10^3 \text{W/(M.K)})\) and electrical conductivity \((\sigma=64 \text{mS/cm})\) are good, it is an excellent electrode material. Graphene materials have been widely used in electrocatalytic oxidation technology due to their excellent electrochemical properties such as good conductivity and minimal resistivity.

### 2.3. Sample Source

The sample is domestic sewage, taken from the septic tank of a residential area in Beijing. The PH is 7.49–8.65, \(\text{COD}_C\) is 157–224mg/L, \(\text{NH}_3\)-N is 59.7–61 mg/L, TN is 65.9–68.6mg/L, the electric conductivity is 1456–1478μs/cm.

### 2.4. Experimental Apparatus

The electrocatalytic oxidation technology device consists of electrolytic cell, anode (graphene electrode), cathode (stainless steel), circulating water tank, inlet water pump, circulating water pump and DC power supply. The effective working area of each electrode is 6 cm × 6 cm, and there are 10 plates in total. The total effective working area is 6cm × 6cm × 10 = 0.036m² and the distance between each two electrode plates is 3mm. The electrochemical oxidation system devices such as Figure 1.

![Figure 1. Schematic Diagram of Non-circulating and Circulating Water Tank Device](image)

### 3. Experimental Content

#### 3.1. Results of Different Current Densities

Add 2g/L of sodium chloride to the domestic sewage, adjust the current density to 500A/m², 600A/m², 700A/m², 800A/m², and adjust the flow rate so that the device residence time is 1min and 2min respectively, Contrast removal effect.

#### 3.1.1. Treatment effect of different current densities at residence time of 1 min

![Figure 2. COD, Ammonia Nitrogen, TN Variation under Different Current Densities](image)
Figure 3. PH and Electric Conductivity Variation under Different Current Densities

It can be seen from the above figures that the higher the current density is, the better the removal efficiency of COD, ammonia nitrogen and TN is, and the lower the electric conductivity of water is. TN removal was slightly lower than ammonia nitrogen removal, and 96.88% of ammonia nitrogen is converted to nitrogen on average. COD, ammonia nitrogen and TN can be removed by electrocatalytic oxidation technology device.

3.1.2. Treatment Effect of Different Current Densities at Residence Time of 2 min

Figure 4. COD, Ammonia Nitrogen and TN Variation under Different Current Densities

Figure 5. PH and Conductivity Variation at Different Current Densities
It can be seen from the above figures that the higher the current density is, the better the removal efficiency of COD, ammonia nitrogen and TN is, and the lower the electric conductivity of water is. TN removal is slightly lower than ammonia nitrogen removal, and 93.87% of ammonia nitrogen was converted to nitrogen on average.

The treatment effect is enhanced when the residence time is increased with the constant current density. Under 2 min residence time, when the current density is 500 A/m² and 800 A/m² separately, COD are less than 100 mg/L in produced waters, their ammonia nitrogen are less than 15 mg/L.

3.2. Continuous Experiments with Salt
Add 1g/L of sodium chloride to the domestic sewage, connect the circulating water tank to the electrocatalytic oxidation technology device, and adjust the current density to 500A/m². Fill the circulating water tank and the equipment with domestic sewage, turn on the electrocatalytic plate power supply (steady current operation), run for 88 minutes, and then get sample for testing. Then turn on the water inlet pump, run for 2.5 hours, and take samples every 30 minutes.

Through self-circulation, the removal rates of COD and ammonia nitrogen are 100% and 98.09% respectively (Long self-circulation time causes complete degradation of COD and ammonia nitrogen). After continuous operation for 1 h, the results are basically stable. The ammonia nitrogen removal rate
is about 97.86%, and the COD removal rate is about 64.29%. The average COD of produced water is 72.5 mg/L, and ammonia nitrogen is 1.35 mg/L.

3.3. Continuous Experiments without Salt

The circulating water tank is connected to the electrocatalytic oxidation technology device, and the flow rate of the pump is adjusted so that the residence time is 20 min and 36 min respectively. It runs continuously at the maximum current for 2 days. During these two days, samples were taken four times during the day.

3.3.1. Treatment Effect at Residence Time of 20 min

Under the current density of 190 A/m² and theoretical residence time of 20 minutes, the equipment does not reach an equilibrium state within 6 hours, and reaches a stable state between 6 and 23.2 hours. The removal rate of ammonia nitrogen is about 97.22%, the average value of ammonia nitrogen in produced water is 1.7 mg/L, and the removal rate of ammonia nitrogen is 59.3 mg/L. The removal rate of COD is about 74.55%, the removal amount of COD is 167 mg/L, and the average value of COD in produced water is 57 mg/L. The proportion of ammonia nitrogen converted to nitrogen is 97.27%.
3.3.2. Treatment Effect at Residence Time of 36 min

Under the current density of 190A/m² and theoretical residence time of 36 minutes, the equipment does not reach an equilibrium state within 6 hours, and reaches a stable state between 6 and 21.8 hours. The removal rate of ammonia nitrogen is about 98.93%, the average value of ammonia nitrogen in produced water is 0.65mg/L, and the removal rate of ammonia nitrogen is 60.35mg/L. The removal rate of COD is about 77.34%, the removal amount of COD is 121.4mg/L, and the average value of COD in produced water is 35.57mg/L. The proportion of ammonia nitrogen converted to nitrogen is 95.11%.

3.4. Electrode Plate Cleaning
The pickling process is the key to the entire chemical cleaning. After the plates are deposited, they are cleaned with 2% hydrochloric acid and 2% citric acid respectively.
3.4.1. Effect of hydrochloric Acid Cleaning

Hydrochloric acid is very fast to clean the electrode plate, soaking for about 20 minutes, the scale of the electrode plate can be completely dissolved.

The electrode plate cleaning speed with 2% hydrochloric acid is fast. However, hydrochloric acid is a precursor chemical and it is very dangerous to use. The purchase, transportation, use, and storage of hydrochloric acid must comply with relevant national laws and regulations such as the Regulations on the Management of Dangerous Chemicals. Purchase should be recorded in the local public security bureau, and then apply for a precursor drug record certificate approved by the local public security agency, finally purchase it from a qualified manufacturer. Storage and use also need to meet relevant high requirements and cumbersome standards, and decentralized sewage treatment stations often do not have these storage and use abilities; Therefore, it is of great significance to check the feasibility of using citric acid instead of hydrochloric acid for pickling. Citric acid as a safe cleaning agent has been widely used in chemical cleaning. As a safe cleaning agent, citric acid has become an important part in the field of chemical cleaning and is widely used in various industries because of its advantages of safety, convenience, non-toxic and low corrosion to metals.

3.4.2. Effect of Citric Acid Cleaning

Citric acid soaking can remove deposition, but the reaction is slow and the efficiency is low. There are still some scale residues after soaking for 16.5 h.

Pour 2% citric acid into the circulating water tank, turn on the circulating pump, observe The removal effect of deposition after 2 hours of continuous circulation.
After 2% citric acid circulates for 2 hours, the deposition on the electrode plate is completely removed. It shows that the cycle operation is much better than the simple immersion effect.

4. Conclusions
1) The addition of salt helps the electrocatalytic reaction to proceed, and the electrocatalytic equipment can remove COD and ammonia nitrogen in domestic sewage.
2) The rapid rise of water temperature is common in the test, and the increase of cooling circulation system can effectively avoid the problem of temperature rise.
3) As the reaction proceeded, the conductivity gradually decreased because part of the chloride ions are electrolyzed into chlorine gas.
4) Ammonia nitrogen degradation is better than COD’s.
5) Extend residence time contributes to the degradation of COD and ammonia nitrogen.
6) In the experiment, about 95.11% ~ 97.27% of the removed ammonia nitrogen was converted to nitrogen.
7) Polar plate deposition can be cleaned by 2% hydrochloric acid and 2% citric acid. Compared with hydrochloric acid immersion cleaning, citric acid has a slower cleaning speed and has residues, but the plate deposition can be thoroughly cleaned by the way of circulating 2% citric acid.
8) Adding sodium chloride 1g/L, keeping current density 500A/m², and residing for 4min for domestic sewage electro-oxidation treatment, the removal rate of ammonia nitrogen and COD is about 97.86% and 64.29% separately. Meanwhile, The average ammonia nitrogen and COD of produced water is 1.35mg/L and 72.5mg/L separately.
9) Without Adding sodium chloride, keeping current density 190A/m², and residing for 20min for domestic sewage electro-chemical oxidation treatment, the removal rate and removal amount of ammonia nitrogen is about 97.22% and 59.3 mg/L separately. The average ammonia nitrogen of produced water is 1.7mg/L. Meanwhile, the removal rate and removal amount of COD is about 74.55% and 167mg/L separately. The average COD of produced water is 57mg/L.

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