

Research Progress in Modification of Electrocatalytic Activated Carbon Electrodes

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Abstract

Activated carbon is widely used as an electrode material for electro adsorption due to its rich pore structure and huge specific surface area. This article reviews the principle of electro adsorption treatment, the pore structure characteristics of activated carbon, common methods and latest research results of activated carbon modification, and prospects the development trend of activated carbon modification technology in water treatment.

Keywords

Activated Carbon; Electrode Modification; Water Treatment.

1. Introduction

The situation of water resources in China is severe. Traditional desalination methods include distillation, ion exchange, reverse osmosis, and electrodialysis, but these methods have certain limitations: high distillation energy consumption and low water production; Ion exchange can generate secondary pollution; The membrane treatment of reverse osmosis and electrodialysis has high investment and cumbersome maintenance [1]. The electric adsorption technology for treating wastewater has the characteristics of low energy consumption, high treatment efficiency, and environmental friendliness, which is conducive to achieving social construction of "carbon neutrality".

2. Electro Adsorption Treatment Method

Electroadsorption technology is a new type of water treatment technology, which has become a research hotspot in water treatment technology, especially in desalination. The electro adsorption technology for wastewater treatment has the advantages of safety, simplicity, low energy consumption, and no secondary pollution, and the industry is paying increasing attention to it. Electrosorption technology (EST) combines electrochemical theory with adsorption separation technology. EST can be used for desalination, hardness removal, seawater desalination, heavy metal wastewater treatment, and advanced treatment of drinking water. EST has unique advantages in processing efficiency, adaptability, energy consumption, operation and maintenance, and environmental friendliness, and has a wide range of applications and development prospects[2].

Electrosorption desalination technology utilizes the surface of charged positive and negative electrodes to adsorb anions, cations, and charged particles in water, enriching and concentrating dissolved salts and other charged substances on the electrode surface to achieve salt removal and water purification. The principle of EST desalination is shown in Figure 1. As shown in Figure 1, when saline wastewater flows in the space composed of positive and negative electrodes, charged particles (ions, colloidal particles, organic matter, bacteria, etc.) in the water are subjected to the action of electric field force. The charged particles move towards the electrodes with opposite charges, are adsorbed by the electrodes, and stored in a double layer, achieving the separation of charged particles (impurities) from water. When the

electrode loses power or is momentarily reversed, charged particles enriched on the electrode fall off and are washed away under the combined action of water flow and electric field force, resulting in electrode regeneration. Do not number your paper: All manuscripts must be in English, also the table and figure texts, otherwise we cannot publish your paper. Please keep a second copy of your manuscript in your office. When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question[3].

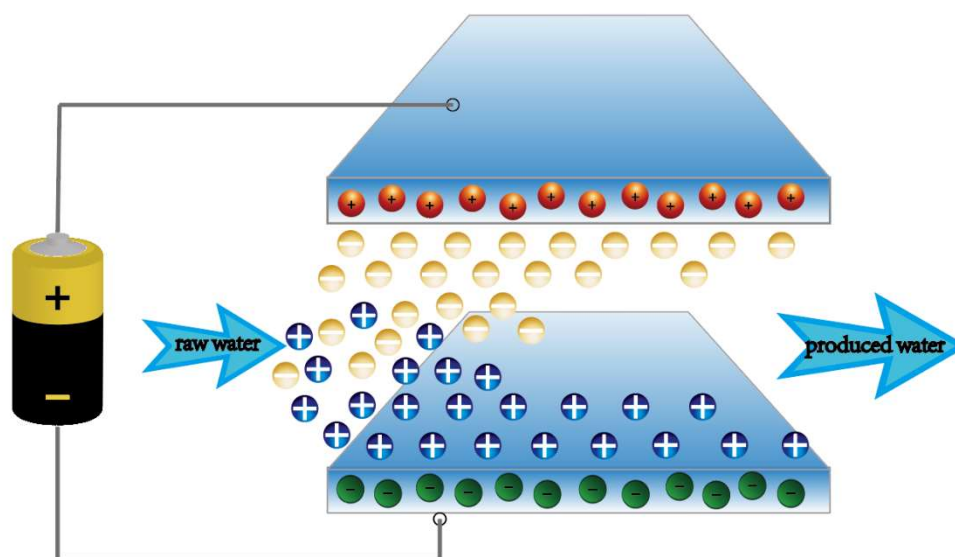


Fig. 1 Schematic diagram of electric adsorption water treatment

3. Electroadsorption Electrode Materials

Electrode material is a key factor affecting the efficiency of electrochemical treatment. An ideal electrode material should have advantages such as large specific surface area, high chemical and electrochemical stability, low contact resistance, high hydrophilicity, and low cost. The electrode materials at home and abroad mainly include graphite electrode, activated carbon electrode, activated carbon fiber electrode, carbon aerogel electrode, carbon nanotube electrode and other carbon electrode materials [4]. Various types of carbon materials have been developed as electrode materials for electro adsorption. Among them, activated carbon (AC), as the most commercially applied porous carbon material, is the first electrode material to be used for electro adsorption. Activated carbon electrodes have developed pore structures, huge specific surface area, and strong adsorption capacity, making them often used as electrode materials for electro adsorption.

4. Characteristics of Pore Structure of Activated Carbon

Activated carbon is a microcrystalline carbon substance prepared through a series of process operations such as carbonization and activation of carbonaceous raw materials such as wood and coal. It has a black appearance and different pore structures inside. Activated carbon has a well-developed pore structure. The disorderly arrangement of pores on the surface of activated carbon provides a huge specific surface area. Generally, pores are divided into three types based on their diameter: micropores with pore sizes less than 2nm Mesopores of 2-50nm and macropores of greater than 50nm. Among them, micropores play a major role in adsorption, and the adsorption capacity largely depends on the number of micropores. In aqueous

electrolytes, micropores with a pore size range of 2-4 times that of adsorbate ions and a diameter greater than 0.5 nm are most favorable for adsorbing the electrolyte to form a double layer, while micropores with a pore diameter of more than 0.7 nm can be entered by most organic electrolytes [5]. In addition, mesopores can serve as channels in the process of electrolyte migration. In addition, activated carbon forms some oxygen-containing functional groups on its surface during the preparation process, and the types of these functional groups also affect the hydrophilic and hydrophobic properties of activated carbon, thereby affecting its adsorption effect on polar and non-polar substances.

5. Modified Activated Carbon

5.1. Physical Activation Modification

The physical treatment of carbon materials generally involves the removal of ash through methods such as gas, sound waves, and heating. The sound wave method is mainly divided into ultrasonic oscillation method, microwave oscillation method, etc. The gas method mainly involves introducing activated gas into the treated material to modify the electrode material, such as water vapor, CO₂, NH₃, N₂, etc. The heating method mainly utilizes a certain temperature to cause the movement and detachment of impurity molecules adsorbed in the material [6]. Physical pre-treatment does not cause secondary environmental pollution, but gas and acoustic methods have higher requirements for experimental instruments and are not as effective as chemical treatment, resulting in unsatisfactory experimental results. Although heating methods have certain applications, they are only used as pre-treatment and not as a critical step. Therefore, physical activation treatment alone has relatively few practical applications.

5.2. Metal and Metal Oxide Modification

Metal oxide composite carbon electrode materials have broad development prospects, and transition metal oxides are currently being studied extensively. Transition metal oxides, due to the multiple oxidation states of metal atoms, can mostly undergo rapid oxidation-reduction reactions under external voltage, thus producing high capacitance. Therefore, they are a promising electrode material [7]. Due to the small size and surface effects of nanomaterials, the active materials in chemical power sources are directly related to these effects. It can be seen that as an electrode active material, an increase in surface area will reduce current density and polarization, leading to an increase in discharge capacity, making it possible to have good electrochemical activity. The common methods for making activated carbon electrodes from metals and metal oxides on the market are as follows:

(1) Low-temperature solid-state synthesis method

Solid phase synthesis method refers to the method of directly mixing solid reactants and obtaining products through chemical reactions through grinding. Compared with other methods, this method has the characteristics of high yield, no solvent required, good reaction selectivity, and low environmental pollution. It can reduce the shortcomings caused by intermediate steps and high-temperature reactions, such as particle aggregation, long crystallization time required, impure products, and low yield. It proposes an inexpensive and simple new method for the synthesis of nanomaterials. However, manganese dioxide is sensitive to experimental conditions such as temperature and grinding. Therefore, it is currently difficult to synthesize single crystal nano manganese dioxide with high purity and low aggregation.

(2) Sol gel method

The sol gel method is to use inorganic salts or metal alkoxides as precursors, gradually gel through the hydrolysis condensation process, and then make corresponding post-treatment to

obtain powder materials. The product obtained by the modified method has good chemical uniformity, high purity, and fine particles. However, the gel process of the system is slow, the synthesis cycle is long, and agglomeration occurs during the calcination process.

(3) Microemulsion method

The microemulsion method is to form a micro lotion from metal salts and certain precipitators, control the nucleation and growth of colloidal particles in a small reaction zone, and finally obtain nanoparticles [8]. This method is simple to operate, easy to achieve continuous production, and the resulting product has controllable particle size, good particle dispersion, narrow distribution, and obvious advantages. It shows extremely broad application prospects in many current methods for preparing nanoparticles.

By using metal oxides to modify activated carbon, the conductivity of activated carbon is enhanced, which is more conducive to the formation of a double layer on the surface of the carbon electrode and improves the electro adsorption capacity of activated carbon.

5.3. Acid and Alkali Modification

According to the properties of functional groups, the acidic functional groups on the surface of electrode materials can enhance the adsorption of polar substances by the electrode, while the alkaline functional groups can enhance the adsorption of weakly polar or non-polar substances by the electrode. Acidic treatment of activated carbon can enhance the content of acidic functional groups on its surface, improve its surface hydrophilicity, and facilitate the adsorption of polar compounds. Alkaline treatment can increase the specific surface area and micropore rate of activated carbon. Sodium chloride is a polar molecule with the chemical formula NaCl, composed of Cl⁻ and Na⁺ ions. These two ions have different electron attraction, so the common electron pair leans towards the Cl⁻ side due to different forces, resulting in it being a polar molecule itself [9]. Therefore, using acidic treatment can improve the adsorption effect of materials on chloride ions.

The research by Fan Yanzhen et al. [10] shows that after oxidation of activated carbon with HNO₃, the content of hydrophilic groups such as carboxyl groups on its surface increases, which is unfavorable for the adsorption of hydrophobic substances by activated carbon. At the same time, the oxidation of concentrated HNO₃ also causes the structure of activated carbon to collapse and the specific surface area to decrease. Although this reduces the adsorption performance of activated carbon for organic substances such as phenol, aniline, humic acid, chloroform, and carbon tetrachloride in water, it significantly increases its adsorption capacity for metal ions such as Pb²⁺. The acid and alkali modification method is simple and feasible, especially the nitric acid modification effect is obvious. Nitric acid modification increases the number of hydrophilic functional groups such as hydroxyl and carboxyl groups on the surface of activated carbon. They act as hydrophilic substances in aqueous solution and promote ion adsorption through ion exchange reactions, thereby improving the selectivity and adsorption ability of activated carbon for hydrophilic substances in solution.

5.4. Plasma Modification

Plasma surface modification is the use of plasma interactions between ions, electrons, and active particles on the surface of activated carbon to alter its microscopic physical and chemical properties while maintaining its excellent performance [11]. Plasma modification has the characteristics of high efficiency and environmental friendliness, and is an emerging technology for modifying activated carbon. It can change the pore structure and surface functional groups according to different plasma conditions. Jiang Hao et al. investigated the adsorption of benzene series compounds with different polarity on low-temperature plasma modified activated carbon, and the results showed that the modified activated carbon fiber significantly increased the specific surface area and micropore volume, and improved the adsorption performance for

ortho xylene, meta xylene, and para xylene. Plasma modification technology changes the surface chemical properties of activated carbon without changing its interfacial properties, making it superior to traditional modification technology. However, due to the high operating cost and difficulty in controlling plasma technology, it is limited in some applications.

6. Conclusion and outlook

The selection of electrode materials is the main factor that determines the deionization effect, energy consumption, and treatment cycle of electro adsorption technology. However, there are still some problems with the current modification methods, such as the difficulty in adjusting the pore structure through secondary activation; Multiple cyclic tests can result in a decrease in specific capacitance retention rate; The problem of electrodes being oxidized during operation, therefore, using a comprehensive modification method that combines multiple methods and steps to develop simple electrode materials with good conductivity, large specific surface area, and stable operation, will become a focus and hotspot of research in the near future. With the emergence of new carbon electrode materials and processes, as well as the improvement of existing processes and mass transfer conditions, the application prospects of electro adsorption water treatment technology will be broader.

Acknowledgments

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