Research on optimization test of electrode material in desulfurization wastewater purification system of coal-fired power plant

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Abstract. The traditional coal-fired power plant wastewater treatment technology is faced with the problems of complex system, high operating cost, easy scaling and corrosion, etc. Therefore, coal-fired power plants need to adopt an integrated multi-functional coupling system, taking into account the desalination, anti-scaling, etc. function to remove pollutants from wastewater. Electro-adsorption technology is a technology that can realize water purification and water desalination. It is a new type of water treatment technology. It can effectively remove impurity ions in water without scaling under the premise of low energy consumption. In this paper, the development history of electrosorption theory, the principle of electrosorption, the main points of electric double layer theory, the structure of electrosorption and its working process are reviewed. Several main electrode materials and their advantages and disadvantages are introduced in this paper. Based on the increasingly stringent environmental protection requirements, electro-adsorption technology is expected to be widely used in the power industry due to its advantages of low energy consumption, low cost, and no secondary pollution.

Keywords. thermal power plant wastewater purification electrode material

1. Introduction

The quality and quantity of waste water from thermal power plants vary greatly. The pollutants in the waste water discharged from thermal power plants are mainly inorganic substances, and the discharge time of thermal power plants is intermittent. The wastewater in the power plant mainly includes desulfurization wastewater, equipment flushing wastewater, ash flushing wastewater and oily wastewater, etc[1]. The wastewater treatment methods are generally aeration oxidation, acid-base neutralization and coagulation clarification. In the "Guidelines for Feasible Technologies for Pollution Prevention and Control of Thermal Power Plants", which was officially implemented, specific treatment methods for desulfurization wastewater were clearly formulated. In the near-zero discharge technology of wastewater, it is emphasized that, except for desulfurization wastewater, all kinds of wastewater can basically achieve "multiple uses of one water, cascade utilization" after treatment, and no wastewater is discharged. Therefore, the key to achieving near zero discharge of wastewater is to achieve zero discharge of desulfurization wastewater [2]. In recent years, electro-adsorption technology, also known as capacitive deionization technology, has attracted widespread attention. In this paper, the development history of electrosorption technology is reviewed, and the principle, structure, adsorption materials and development trend of electrosorption are introduced [3].

2. Treatment of waste water from thermal power plants

2.1. Production wastewater

The industrial waste water of thermal power plants includes industrial cooling water, filter backwash waste water, boiler cleaning waste water, coal conveying washing and dust removal waste water, cooling tower sewage waste water and oily waste water, etc. There are many types of industrial waste water. The discharge and content of pollutants in wastewater are not fixed values, and the components in various wastewaters are relatively complex. If this type of waste water is directly discharged, it will bring different degrees of pollution to the environment, and also bring serious damage to the ecology. Therefore, thermal power plants should save water and reduce the water consumption of thermal power plants. Thermal power plants should improve the efficiency of water reuse and reduce environmental pollution [4]. Generally, the waste water of thermal power plants will be reused after treatment, and zero discharge of waste water will be realized according to government requirements. Boiler scheduled discharge and ash removal air compressor cooling water discharge sewage: This kind of sewage is uniformly collected in the recycling water pump room, after being lifted by the water pump, filtered and processed, and then replenished into the raw water storage tank of the chemical water treatment workshop, thereby replacing part of the industrial Use water.See Figure 1.

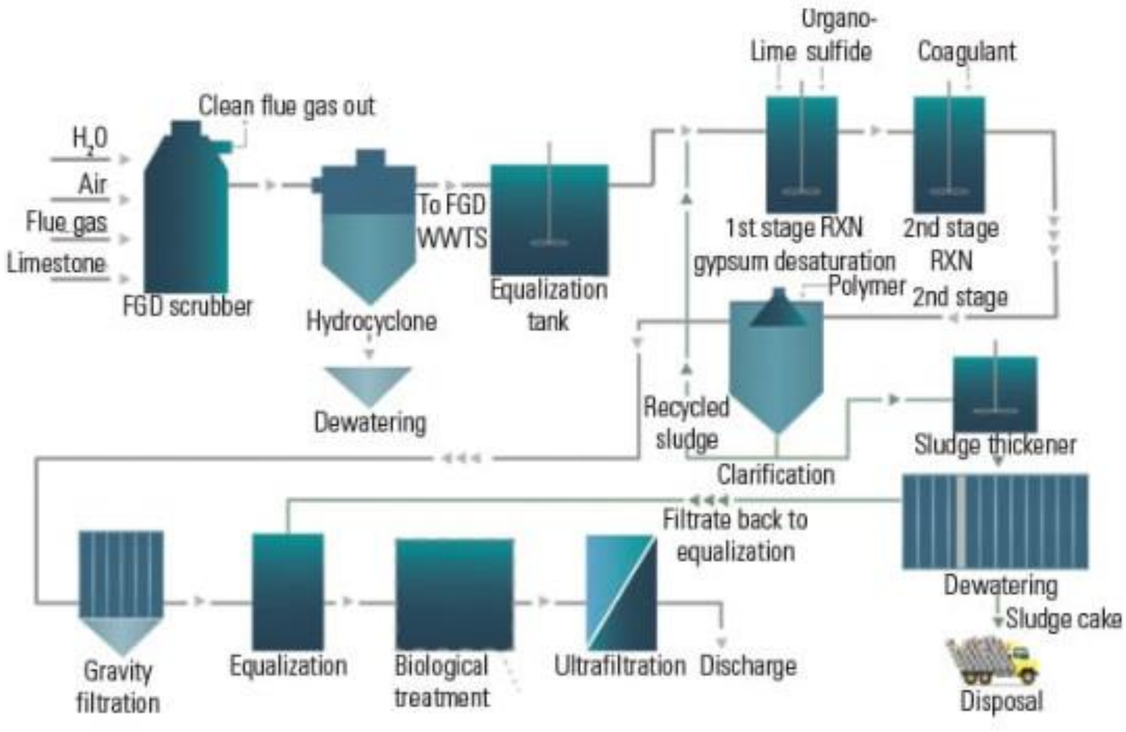

Figure 1. Thermal power plant wastewater treatment process

Circulating water and sewage: After the water quality of the circulating water is evaporating and dissipating heat from the cooling tower, the overall salt content of the water is too high, and other water quality changes little, and part of the wastewater is discharged to the pump room for reuse of water in the plant area. It can be used for coal washing or coal yard spraying, ash removal and other applications. Coal conveying flushing and drainage: This type of water is collected into the coal water treatment room, and then reused after being treated by special water treatment equipment. Chemical drainage: The drainage from the chemical reverse osmosis device is recycled to the pump room like the circulating water, and is used for flushing water in the coal conveying system, spraying water in the coal yard and replenishing water in the ash removal system. Drainage from the chemical neutralization pool and oily wastewater from the plant are fed into the wastewater treatment station for further pH adjustment and reused as service water.

2.2. Flush grey water

Ash flushing water is one of the main sewage in thermal power plants. It is generally used to flush coal slag or to discharge ash from dust collectors. Ash flushing water accounts for about 50% of the entire thermal power plant wastewater. There are many types and contents, and the pollution to the environment is relatively serious. Even some thermal power plants contain heavy metals and arsenic. This type of water is strictly prohibited from being directly discharged into the environment, otherwise it will seriously damage the organisms in the water. chain, and the soil rapidly becomes salinized. In the treatment of flushing water, its pH value is treated. Thermal power plants use acid to neutralize the alkalinity of flushing water, and some thermal power plants use circulating water for dilution. Usually, the recovery rate of flushing water is 50% or so. Thermal power plants differentiate between acidic and alkaline grey water according to the nature of the water, and then treat the flushed grey water according to different methods. See Figure 2.

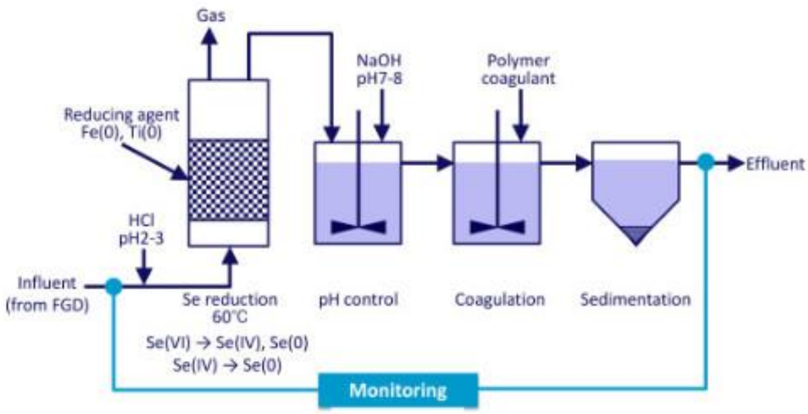

Figure 2. Method for purifying waste water in thermal power plant

3. Method for purifying waste water in thermal power plants

For the removal of heavy metals in wastewater, thermal power plants mainly use chemical precipitation, adsorption, ion exchange, membrane separation technology to purify wastewater. However, these methods have problems such as insufficient removal capacity, high cost, and easy to cause secondary pollution. In contrast, capacitive deionization technology has gradually attracted the attention of scholars at home and abroad due to its low energy consumption, low cost, easy recycling, and no secondary pollution. The key to capacitive deionization technology is the electrode material. The ideal electrode material should have the advantages of good electrical conductivity, abundant pore distribution, large specific surface area and good wettability. Among them, electrode materials include activated carbon, graphene, carbon nanotubes, template carbon, etc. Carbon materials have become a hot spot in electrode material research due to their large specific surface area and abundant pores. Although activated carbon has abundant pores and is one of the most commonly used electrode materials, its main pore size is micropores, which limit the transport of ions and greatly affect its capacitive deionization performance. Compared with the disordered activated carbon materials mainly composed of micropores, the porous carbon prepared by the template has a highly ordered mesoporous grid structure, which can better serve as a channel for ion transport. The mesoporous mesh structure improves the ion diffusion effect by reducing the ion diffusion distance, ensures that the internal resistance of the ion transmission path is minimized, and has a better adsorption effect for ions in solution. But at the same time, it should be noted that the main adsorption form of porous carbon is the undifferentiated physical adsorption inside the pores of the carbon material, which lacks the selective removal ability of ions. In the water sample environment where a large number of high concentrations of salt coexist, due to competition the interference of ions will weaken the removal effect of related heavy metal ions. Therefore, thermal power plants need to develop an electrode material capable of selectively removing heavy metal ions through an electrosorption process, which is a challenge. See Figure 3.

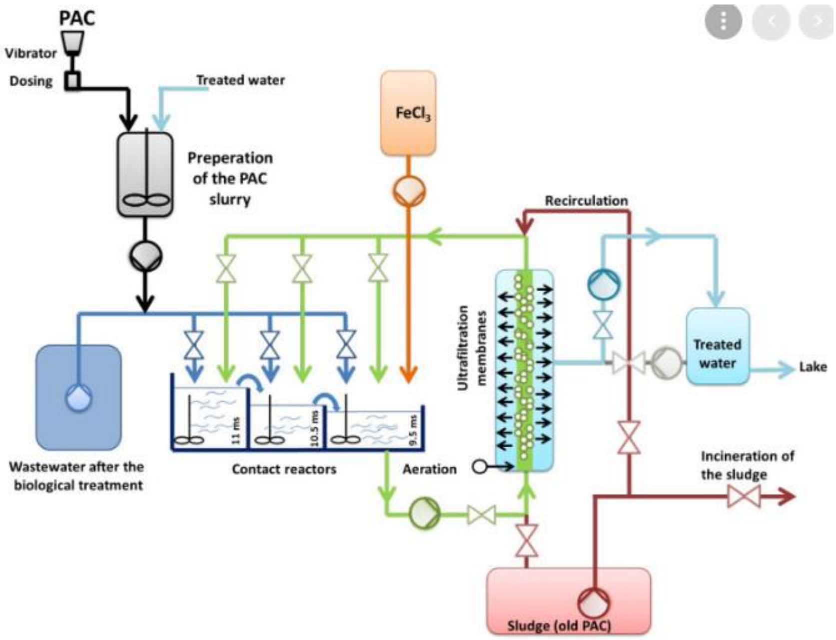

Figure 3. Electro-adsorption technology for waste water purification in thermal power plants

4. Electrosorption technology

Electrosorption technology is to use the charged electrode surface to adsorb water ions and charged ions, so that the substances in the water are concentrated and enriched on the electrode surface, so as to achieve high-efficiency and energy-saving low-salt or medium-salt water desalination technology. The electrosorption process is divided into two parts: adsorption process and desorption process. When the wastewater to be treated in thermal power plants passes through the porous electrodes, it will be subjected to the electric field force applied by the system. When the charged charges on the electrodes enter the solution, the ions in the solution are redistributed and arranged. At the same time, under the action of Coulomb force, the interface between the charged electrode and the solution is occupied by counter ions, and the change of the residual charge at the interface will cause the change of the interface double-layer potential difference, thereby forming a dense electric double layer at the electrode and electrolyte interface. The anions and cations in the solution gradually migrate to the electrode plates with opposite polarities, and the ions are adsorbed on the surface of the material to achieve the purpose of removing pollutants. With the progress of the chemical reaction, the ions adsorbed on the electrode surface are saturated, and the technicians need to desorb and regenerate the adsorbent material. Thermal power plant technicians generally use the polarity reversal or short-circuit method for desorption, so that the ions adsorbed on the surface of the material are released into the solution through the repulsion of the electric field, and finally produce concentrated water and discharge to achieve desorption.

5. Electrode adsorption materials and basic theory

The adsorption material is mainly carbon material, which has the advantages of large adsorption capacity, good regeneration effect, low price and easy availability. Commonly used electrode materials include activated carbon, graphene, carbon aerogel, etc. A good electrode adsorption material should have a large specific surface area. The excellent electrode adsorption material has good chemical stability during normal operation, the ions in the solution have high mobility in the pore size, and the electrons have good conductivity in the electrode material. Excellent electrode materials have good wettability, low cost, and scalability. Excellent electrode materials have good processability, large specific surface area, and high biological inertness.See Figure 4.

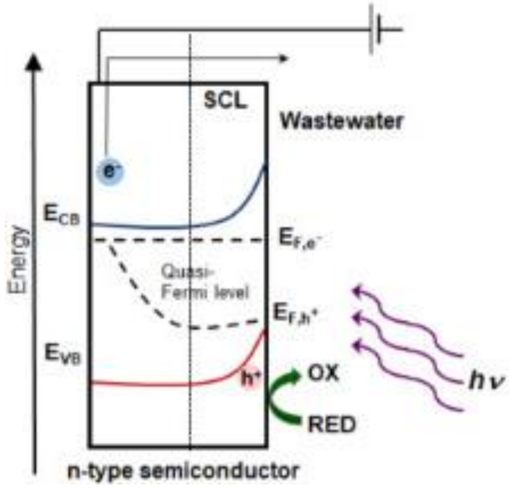

Figure 4. Electrode Adsorbent Materials and Basic Theory for Wastewater from Thermal Power Plants

5.1. Activated carbon

Activated carbon and activated carbon cloth are the most widely used porous carbons, and their use has been demonstrated in early studies of capacitive deionization technology in the 1960s and 1970s. Activated carbon is a common porous carbon material with developed pores and large specific surface area. In addition, the raw materials for preparing activated carbon are various and the cost is low. Large-scale industrial production has already been realized, and now it is widely used in many fields. Activated carbon is mostly used as an adsorption material in production and life. For example, in the sugar industry, the adsorption of activated carbon is used to decolorize liquid sugar, in heavy metal smelting, it is used to adsorb heavy metal ions, and it is used in the wastewater treatment industry. Organic pollutants, which are used in waste gas treatment to adsorb harmful gases such as sulfur dioxide and formaldehyde. The porosity and large specific surface area of activated carbon can also be used for electrosorption desalination during the electrosorption process. However, because the activated carbon on the market often contains a lot of impurities, these impurities not only easily cause the blockage of the pore size of activated carbon and affect the entry of salt ions into the pore size of activated carbon, but also affect the conductivity of the electro-adsorption electrode and reduce the desalination efficiency of electro-adsorption. , increasing energy consumption. Therefore, the impurities in the activated carbon should be removed as much as possible before the activated carbon is applied to the electro-adsorption electrode in the thermal power plant, and the deashing treatment should be carried out.

5.2. Activated carbon cloth

Activated carbon cloth is synthesized from resin-derived acrylates, and most other acrylates are usually powders composed of micron-sized particles. For example, micro-carbon fibers can be obtained by mixing polyacrylonitrile and conductive additives (carbon black). Pore structure is the most important feature of activated carbon, and the salt adsorption capacity can be increased by increasing the ratio of total pore volume/specific surface area.

5.3. Ordered Mesoporous Carbon

Ordered mesoporous carbons have highly periodic hexagonal or cubic arranged mesopores, which can be derived from soft or hard templates. For hard templates, such as zeolites or ordered mesoporous silica, infiltrate with a carbon precursor and then carbonize, and finally chemically remove the initial template (eg, using hydrofluoric acid) to obtain ordered mesoporous carbon; soft templates are a newer type of ordered mesoporous carbon. A method for the synthesis of mesoporous carbon materials, which involves the self-assembly and thermal removal of triblock copolymers, and the only solid-phase carbon left at the end retains the ordered porous character of the template.

5.4. Graphene

As a new type of two-dimensional carbon material, graphene exhibits excellent mechanical and electrical properties based on its unique physical and chemical structure. It has attracted a lot of attention since. The preparation methods of graphene can be roughly divided into three types according to different principles, namely mechanical exfoliation method, chemical vapor deposition method and redox method. The yield of the product obtained by the mechanical exfoliation method is very small and the yield is extremely low. Although the graphene obtained by the chemical vapor deposition method can obtain high purity and has a good application prospect in the development of advanced semiconductor components, the two Due to the limitation of production conditions, it is not suitable for large-scale preparation and production of graphene at this stage, thus restricting the wide application of graphene. In recent years, people have made great breakthroughs in the preparation of graphene by redox methods. Not only can graphene be prepared on a large scale in the laboratory, but graphene preparation has also been commercialized in some places. At present, with the maturity of the method of preparing graphene by redox method, people begin to focus more on the preparation and application of graphene composites. In the process of preparing graphene by redox method, due to the introduction of abundant oxygen-containing functional groups on the graphite sheet, this method greatly enhances the reactivity of graphite, so thermal power plants can use this graphene oxide. The properties are compounded and restored with other materials. And by compounding other materials, the aggregation between graphenes can also be reduced.

5.5. Ion exchange membrane

An ion-exchange membrane is a polymer membrane that contains ion-exchange groups that allow only specific ions to pass through. Ion exchange membranes are widely used in chlor-alkali industry, metallurgy and water treatment industries due to their unique charging characteristics. According to the performance of ion exchange membrane, it can be divided into cation exchange membrane, anion exchange membrane and amphoteric exchange membrane. Since the cation exchange membrane contains acidic active groups such as sulfonic acid groups, phosphoric acid carboxylic acid groups, etc., it can selectively permeate cations and prevent the permeation of anions, while the anion exchange membrane contains primary ammonium, secondary Ammonium group, tertiary ammonium group and other basic active groups, so it can play the role of selectively permeating anions and preventing cation permeation. However, in the electrosorption experiment, if only the formed ion exchange membrane is used to cover the electrode surface by pressure, the contact resistance between the electrode and the ion exchange membrane will increase, and the thickness of the ion diffusion layer will also be increased.

6. Influencing factors of electrode materials for wastewater treatment

6.1. Iron plate

The flocs produced by the electrode plate are small and dense, and settle quickly, but the effluent after the electrode material treatment often turns yellow, and the iron electrode plate is easy to continue to corrode when the worker is powered off. The flocs produced by the aluminum plate are large and loose, and the sedimentation is slow, but it does not produce chromaticity and has strong adsorption capacity. The plate spacing also affects flocculant growth and subsequent flocculation. When the technicians studied the electroflocculation treatment of reverse osmosis concentrated water, they found that the distance between the plates is the main factor affecting the removal of chemical oxygen demand by electroflocculation. If the distance between the plates is too large, the electrolysis efficiency will be low and the concentration polarization will increase; if the distance between the plates is too small, it is easy to cause short circuits and blockage of flocs between the plates, reducing the effective electrolysis area of the plates.

6.2. Current density

Within a certain range, the larger the current density, the larger the amount of flocculant produced, and the higher the electro-flocculation efficiency. However, excessive current density can easily lead to excessive electrode polarization, accelerate electrode passivation, increase plate and power consumption without improving processing efficiency.

6.3. Electrolysis time

If the electrolysis time is less than the optimal reaction time, the electroflocculation process will not produce enough hydroxyl complexes to react with the target contaminants, or neither will have sufficient reaction time. This will greatly reduce the effect of wastewater treatment. However, if the electrolysis time exceeds the optimal reaction time, the removal rate of heavy metal ions from wastewater is basically unchanged, but the energy consumption increases.

7. Improved method of electro-adsorption treatment technology

There are still many defects in the electro-adsorption treatment technology. First, the use cycle of the adsorption material is short and the chemical stability is poor. Second, the electrode resistance is large and the current efficiency is low. In the future, it should be improved from the following three aspects: First, as the adsorption material is the most important part of the electrosorption system, scientific researchers and technicians should focus on the adsorption capacity of the adsorption material. Increasing the adsorption capacity will greatly improve the decontamination capacity of the waste water purification system in thermal power plants and reduce the frequency of regeneration. In addition, the regeneration effect of the adsorbent material, ie the stability of the material, also affects the service life of the system. Second, the electro-adsorption material with special structure can complete the system optimization by increasing the specific electrode area of the reactor, strengthening the mass transfer, and improving the space-time yield of the reactor. Third, electro-adsorption water treatment technology cannot purify some pollutants simultaneously, so it can be integrated with other water treatment technologies or use catalytic electrode materials. Compared with foreign technology development, domestic research on electrochemical water treatment technology still lacks systematicness, and there is still a big gap in domestic electrochemical reactor optimization design and functional coupling.

8. Conclusion

It is an integrated multi-functional coupling system with electro-adsorption as the core. It takes into account the functions of desalination and anti-scaling. It can remove pollutants in wastewater with high efficiency and low energy consumption. It has broad application prospects in the power industry. As the current electroadsorption technology is in the preliminary exploration stage in the power industry, further research is needed on the electrosorption mechanism, prediction model, and adsorption materials. Especially in the treatment of desulfurization wastewater, due to the complex water quality of desulfurization wastewater and the relatively high salt concentration of desulfurization wastewater, it is difficult for thermal power plants to effectively purify desulfurization wastewater by only relying on adsorbent materials, so thermal power plants need to couple other technologies. In general, the removal methods of desulfurization in thermal power plant wastewater are constantly improving and innovating, and there are many types, but most of them are still in the experimental stage, and some methods can be limitedly applied to the treatment of thermal power plant wastewater with small and medium water volumes. It is believed that in the future, with the development of industrialization, the update of technology and the unremitting efforts of scientific researchers, the desulfurization wastewater removal technology will become increasingly mature.

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