

Capacitive deionization technology and its application in circulating cooling sewage treatment: current situation and development trend

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ABSTRACT

The shortage of water resources is an important environmental problem in the development stage in China. Circulating cooling water as an important part of industrial water, it is of far-reaching practical significance to select appropriate water treatment technology for recycling and reusing. As an efficient and energy-saving water treatment technology developed in recent years, capacitive deionization (CDI) technology owns the characteristics of flexible operation, large adsorption capacity, no need for chemical dosing, and a high degree of automation, etc. Thus, it has a broad application prospect in circulating cooling sewage treatment. In this paper, the principle, device structure, workflow, and adsorption materials related to CDI technology are elaborated in detail, and the research progress and application cases of this technology in circulating cooling sewage treatment are introduced. Furthermore, the development prospect of CDI technology in the future is prospected also.

Keywords: CDI technology; Circulating cooling sewage; Water treatment technology; Adsorption materials

1. Introduction

Thermal power plants are the main power generation method in China. The capacity and power generation of thermal power plants account for 80% and 78.72% of the country's total installed capacity and power generation, respectively [1]. Thermal power plants consume a lot of freshwater during power generation. It is reported that water consumption in thermal power plants accounts for 11% of the total industrial water consumption in the

country [2]. Among them, the circulating cooling sewage accounts for a large proportion of water used in thermal power plants, accounting for about 70%–80% of the water used in thermal power plants. Economical and effective treatment and reuse of circulating cooling sewage are good for saving water resources [3]. There are three types of typical pollutants in the circulating cooling sewage: calcium and magnesium hardness, chloride ion, and a small amount of chemical oxygen demand (COD). For a long time, the circulating cooling water sewage is directly discharged into

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the surface water rather than reused as the supplementary water, resulting in a waste of water resources and environmental pollution [4]. In recent years, a variety of new water treatment technologies have been gradually applied to circulating cooling water systems. Common commercial water treatment technologies have been developed to achieve efficient desalination, such as reverse osmosis, electrodialysis, thermal distillation, and multi-stage flash. However, such technologies consume a lot of energy and are not a cost-effective method [5]. In recent years, capacitive deionization (CDI) technology has been widely concerned as a desalination alternative technology due to its advantages of simple design, low energy consumption, economic feasibility, high efficiency, safety, and environmental benign.

CDI is also known as electrosorption technology [6], which is an efficient and energy-saving desalination technology for low or medium saltwater developed in recent years. Its principle is to form an electric double layer (EDL) [7] on the surface of porous electrode materials under the action of the electric field to trap ions from solution. This technique is based on the principle of CDI to separate ions on the surface of charged electrodes usually composed of high-porous carbon materials [8]. CDI can reduce secondary pollution as it can not only increase the adsorption capacity of adsorbent but also regenerate saturated adsorption through potential reversal (or potential withdrawal); compared with traditional regeneration technology, secondary pollution can be reduced. Unlike reverse osmosis and distillation, CDI technology does not require high pressure or high temperature. It can operate at room temperature with a small voltage applied by continuous water flow. The traditional ion-exchange method because of strong acid or strong base reverse washing will bring in other chemical substances, while CDI technology is the direct participation of electrons in the reaction.

In this paper, the principle, device, working process, and adsorbent materials of CDI technology are summarized, and the current situation of the circulating cooling sewage

treatment is analyzed. The application of CDI technology in the treatment of circulating cooling sewage is discussed in detail. In addition, the rationalization of the problems that may arise in the application process is given. The development trend of CDI technology in the treatment of circulating cooling sewage is prospected also.

2. CDI technology

2.1. Principle of CDI technology

The CDI process is divided into an adsorption process and a desorption process, and the principle of CDI is shown in Fig. 1. The presence of electric field forces leads to the potential difference applied by the system when the saltwater passes through the porous electrode. When the charged charge on the electrode enters the solution, the charge is re-distributed and aligned between the electrodes and the different phases of the solution. At the same time, charged electrodes attract ions from the solution. Due to the Coulomb force, the interface between charged electrode and ion-rich solution will be occupied by counter ions, and the change of residual charge at the interface will cause the change of potential difference between the two layers of the interface, forming a dense double layers [9] at the interface between electrode and electrolyte. The anions and cations in the solution gradually migrate to the opposite polarity of the electrode plate, causing ion adsorption and reducing the overall salinity of the water [10], while removing colloidal particles and charged species [11]. As the reaction proceeds, the ions adsorbed on the surface of the electrode are saturated, and the adsorbent material needs to be desorbed and regenerated. Generally, the polarities of the two electrode plates are reversed, so that the ions adsorbed in the dielectric layer are released into the solution by the repulsion of the electric field, and finally, the concentrated water is discharged to complete the desorption. The schematic diagram of desorption principle is shown in Fig. 2.

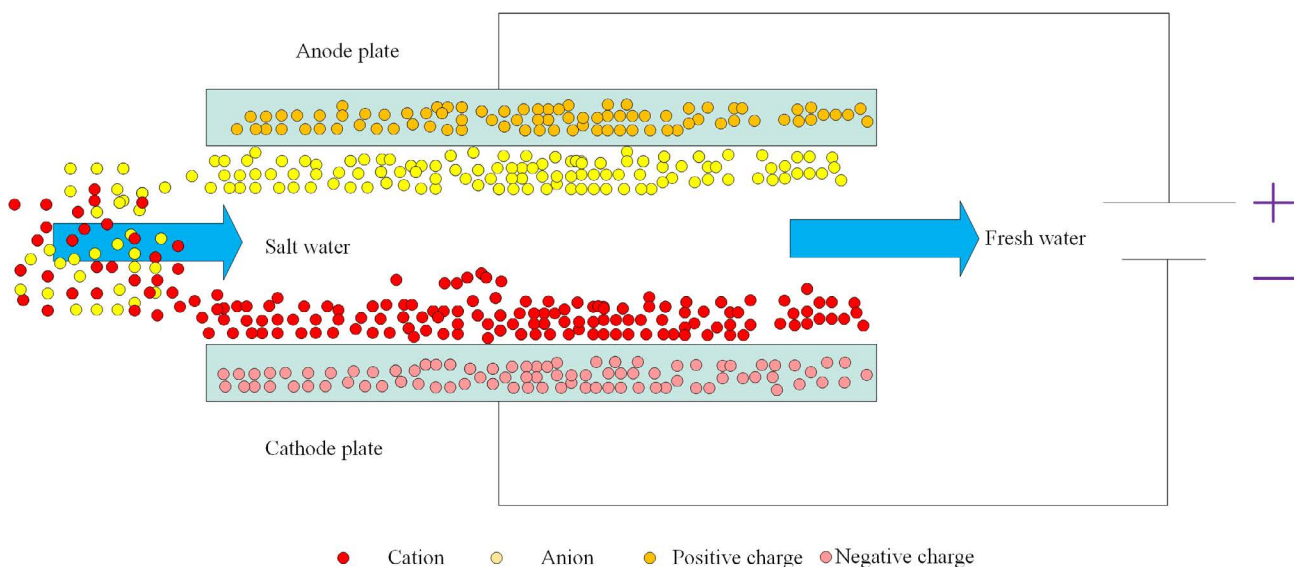


Fig. 1. Schematic diagram of adsorption.

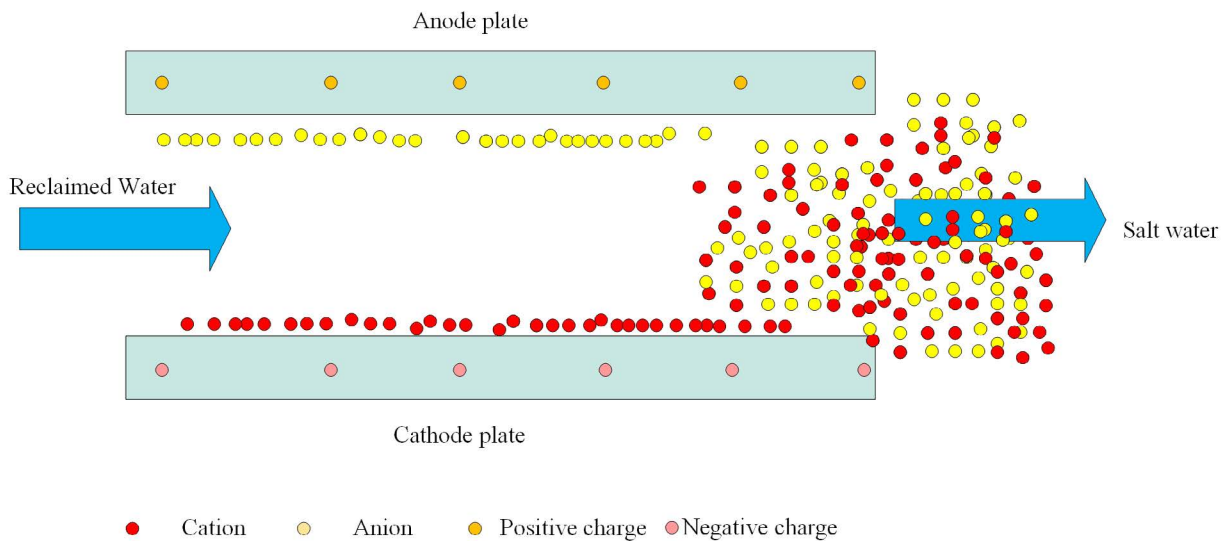


Fig. 2. Schematic diagram of desorption.

2.2. System structure of CDI

CDI systems (as shown in Fig. 3) generally include end plates on both sides, a pair of porous electrodes and netting. In this system, a portion of the charge carried by the electrodes is used to adsorb the opposite ions, while another portion of the charge repels the isotropic ions, resulting in the adsorption efficiency failed to achieve the desired effect. In order to avoid this problem, anion exchange membrane (AEM) and cation exchange membrane (CEM) are added to the conventional device; such a device is also called membrane capacitive deionization (MCDI) [8]. MCDI process flow chart and working process diagram are shown in Figs. 4 and 5, respectively.

As research continues, many innovative structures of CDI have emerged. For example, inverted CDI (i-CDI) [12] is characterized by a net negative surface charge and a cathode with a net positive surface charge. It is completely opposite to the adsorption–desorption behavior of conventional CDI. This structure has a longer service life but insufficient salt removal capacity. The biggest innovation of flow-through CDI [13] is that the feed water directly crosses the electrodes instead of passing between the two plates, and the advantage of this structure is that the mass transfer is improved, and the micropores have higher desalination performance and charging efficiency; however, the required feed pressure will increase. Hybrid CDI (HCDI) [14] is a combination of a battery as an anode or a cathode with the traditional CDI. HCDI can effectively improve the adsorption capacity, but liquid intercalation materials limit its usable range, and imperfect operating characteristics of HCDI system are still obstacles to the development of HCDI [15]. The flow-electrode capacitive deionization (FCDI) process [16] is shown in Fig. 6. The biggest feature of this process is the replacement of a conventional solid-state adsorption electrode with a fluid channel containing a carbon-containing adsorbent material. A voltage is applied between the two collectors of FCDI batteries, and the ions present in the electrolyte

pass through the ion-exchange migration film to the flow electrode, where they are eventually absorbed onto the suspended carbon material.

In the past two decades, the architecture of CDI technology has continuously emerged, which has made great progress in the research and development of CDI [17]. CDI performance depends not only on the design and operating parameters of the device (electrode potential, solution concentration, device volume, flow rate, etc.), but also on the properties of the electrode material (surface area, curvature, porosity, and electrode thickness).

2.3. Electrode adsorption materials

As an important part of CDI, a large number of adsorbent materials have been extensively studied. Current research focuses on porous carbon electrode materials with a specific surface area greater than 1,000 m²/g. Many carbon materials are used as CDI electrodes due to their low cost, high specific surface area, good stability, and non-toxicity [18], such as activated carbon, graphene, carbon spheres, carbon nanotube (CNT), carbon fiber, porous carbon, and carbon-based aerogel, etc.

The adsorbent material is the core component of the electrode adsorption device, and activated carbon powder and particles are mostly used as the adsorption material in the CDI system. Activated carbon has been extensively studied as an electrode adsorption material [19–21]. Caudle and Stern [22] used inert polymeric binders to bond carbon particles together in a conductive sheet and used porous carbon as a downstream experimental device for the electrodes. Johnson and Newman [23] studied the batch process of desalting water in water using two large-area porous carbon electrodes. The results showed that polymer adhesives were often adsorbed to the surface of some activated carbon, which made the electrodes have higher current transfer and mass transfer resistance. Therefore, the CDI device made of activated carbon as the electrode was still far

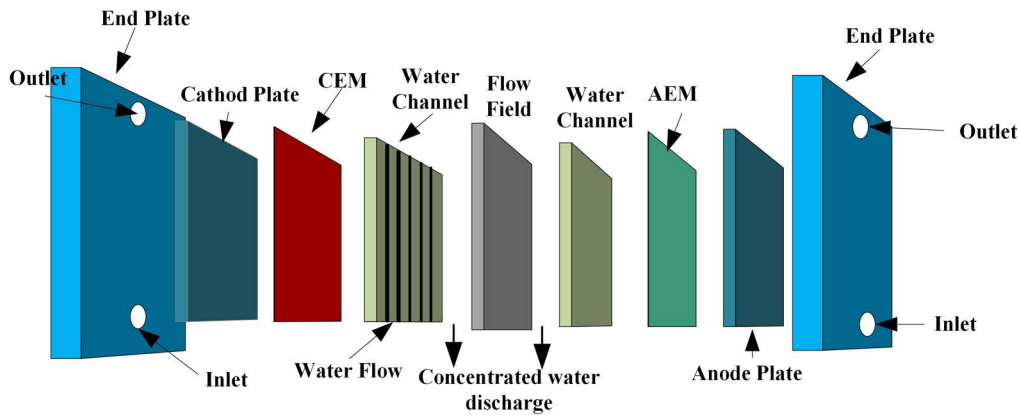


Fig. 3. Structure of MCDI.

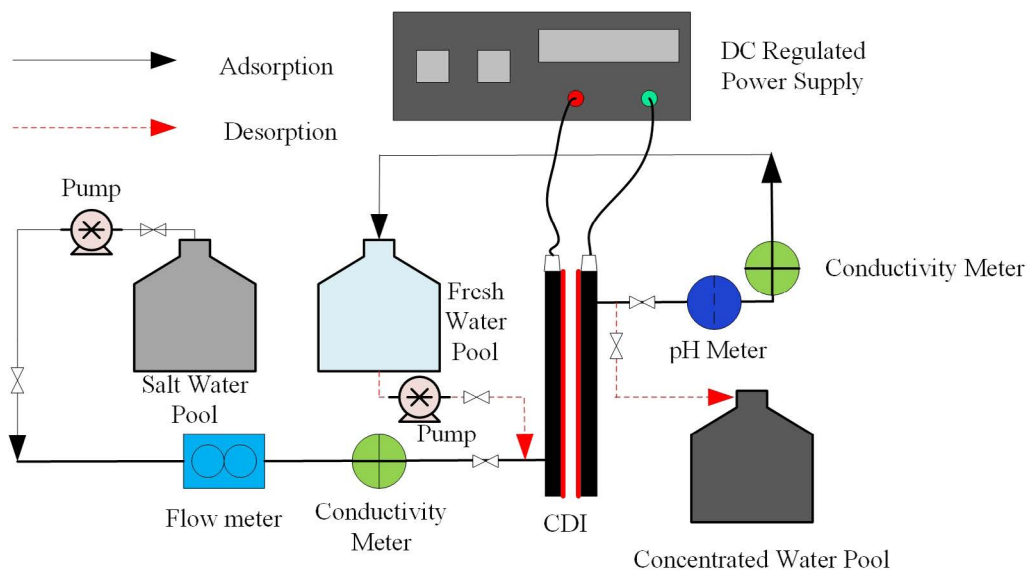


Fig. 4. Flow chart of CDI.

from practical application, but it could be changed through the development of ultra-high specific surface area activated carbon. Liu et al. [24] selected two commercial activated carbon electrodes with raw materials of coal (AC1) and wood (AC2) as electrode adsorption materials, and their physical and electrochemical characteristics were determined by Brunauer–Emmett–Teller (BET) and cyclic voltammetry experiments. The result showed that the CDI performance of AC1 was better than that of AC2, and AC1 was more well-developed to be utilized for the desalination. Thus, a fundamental research for estimating the performance of electrode adsorption materials could be provided through this study.

After the successful development of the Lawrence Livermore National Laboratory in the United States in 1987, the desulfurization of electrosorption electrode materials was carried out. The treated ions were: Na^+ , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , and CO_3^{2-} , having achieved good desalination effect [25,26]. Pekala et al. [27] from the same laboratory prepared a single module for electrode adsorption of carbon aerogel

electrodes and carried out small-scale desalting experiments on NaCl in water. After 1 h, the carbon aerogel electrode was saturated and the solution NaCl was removed. The rate is up to 99%. However, there was no operability in the practice involving higher scale processing.

CNT is characterized by a special hollow structure, high specific surface area, good electrical conductivity, and high stability. They are seamless tubes made of single or multi-layer graphene, which has been regarded as an ideal adsorption material for water treatment equipment in recent years. Wang et al. [28] prepared CNT sponges by chemical vapor deposition to be very flexible and have three-dimensional continuous and mesoporous structures. For the first time, CNT sponges were used as electrodes for CDI. The results showed excellent electrical conductivity and a large specific surface area with a maximum adsorption capacity of 40 mg/g. However, thermodynamics and stability have not been explored. In addition, CDI performance is greatly limited by the powder morphology and ease of aggregation of CNTs.

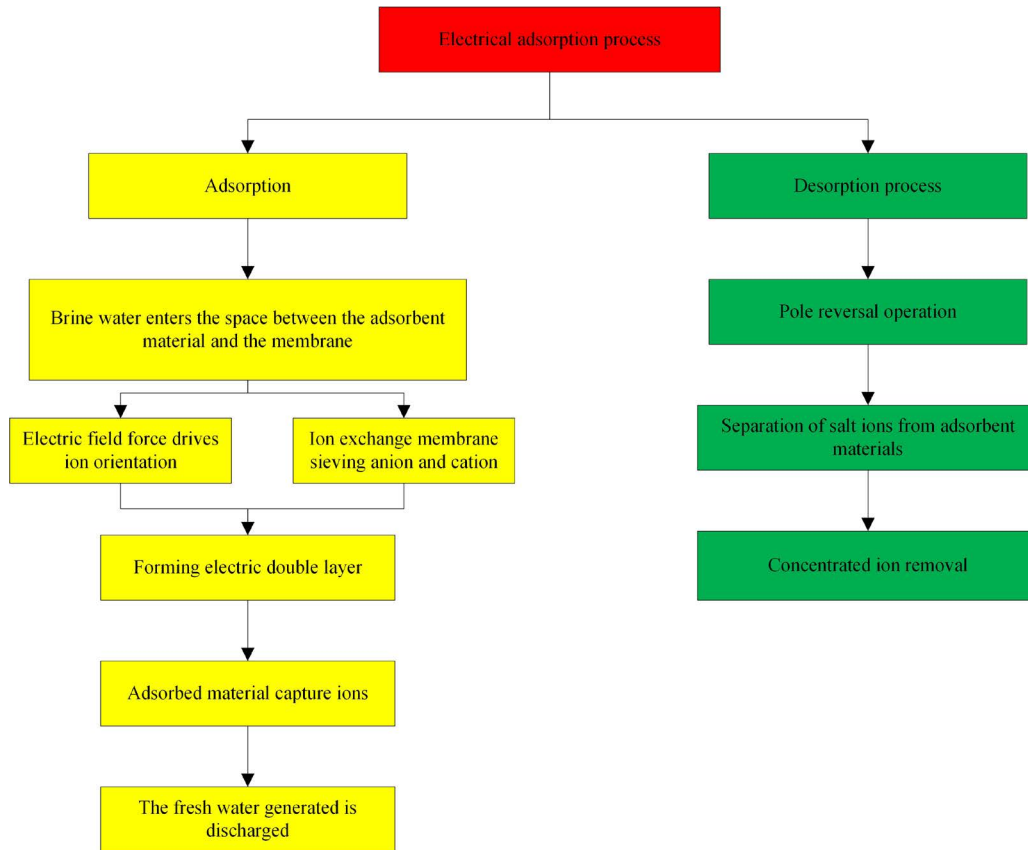


Fig. 5. Working process of CDI.

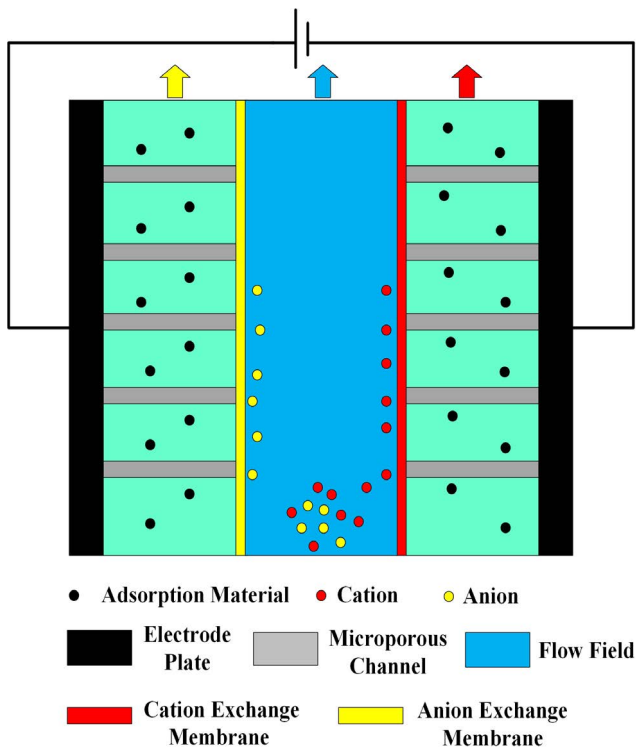


Fig. 6. Structural model diagram of FCEDI.

Graphene is a carbon material that has been gradually developed in the past decade. It is prepared from CNTs and graphite and belongs to a two-dimensional molecular structure with high specific surface area, high conductivity and good chemical stability. The most important thing is that graphene can effectively reduce the cost of CNTs processing and preparation. Related studies have shown that the specific surface area of graphene is difficult to exert desalination independently when the COD in water is high. Li et al. [29] conducted an electrode adsorption study on graphene composites and found that it was difficult to increase the specific surface area by surface modification. When the graphene materials were prepared by chemical or thermal reduction, they would agglomerate the graphene nanocrystals and thus failed to show their proper capacitive adsorption capacity. Zhang et al. [30] prepared graphene/mesoporous carbon (GE/MC) composites by direct triblock copolymer template method and used them as CDI electrodes for the first time. The effects of graphene content on its structural properties and electrochemical properties were investigated. The composite electrode has good performances in capacitance, conductivity, velocity, and cyclic stability.

Modification of carbon materials with metal oxides can effectively increase the specific capacitance of the materials. The addition of metal oxides can significantly change the physical and chemical properties of carbon materials, such as wettability surface area and zeta potential, which may help improve CDI performance [31]. Srimuk et al. [32]

used nano-carbon particles hybridized with sol-gel-derived titanium dioxide to stabilize the material's saturated oxygen content in low molar saline (90% of the initial salt adsorption capacity after 100 cycles). Electrochemical analysis using a rotating disk electrode (RDE) confirmed the oxygen reduction reaction (ORP) effect of the material, which could prevent local peroxide formation by changing the redox reaction. Hand and Cusick [33] modified the carbon aerogel electrode by depositing an amorphous manganese dioxide layer by electroless deposition (ED). The sodium adsorption capacity of the ED electrode increased with the mass deposition of MnO_2 , and the peak charging efficiency could reach 0.95. The presence of MnO_2 also greatly changed the electrode potential required to remove sodium ions, reduced the reduction of oxygen and the reverse desalination cycle, so that the energy release was consistent with the removed salt. These results highlighted that MnO_2 coating plays an important role in improving the desalination ability of carbon electrodes.

In summary, the adsorption materials of CDI are mainly carbon materials, and the advantages and disadvantages of each material are shown in Table 1. Due to the particularity of the CDI technology, the adsorbent material should have the following characteristics [34]:

- good chemical stability;
- large specific surface area;
- pore size is large;
- high conductivity;
- between the adsorbent material and the electrode plate low resistance;
- good hydrophilicity;
- low cost and practicality;
- good processability;
- easy to obtain and environmentally friendly;
- not easily stained by microorganisms.

3. Circulating cooling sewage

Circulating cooling water refers to the heat exchange of the medium through the heat exchanger to exchange the

heat of the medium, and after cooling by the cooling tower, it is recycled to save water resources. The cooling of circulating water is the result of the combined effects of three processes, namely, heat from evaporation, heat from contact, and heat from radiation [35]. The circulating cooling system can be divided into an open circulation system and closed circulation system according to whether the cooling circulating water is directly in contact with the atmosphere. The cooling water system of the power plant is generally an open circulation system (such as counter-flow and cross-flow cooling towers) [36], as shown in Fig. 7. In the open circulation system, the air and water in the cooling tower make full contact. Dust in the atmosphere is constantly mixed into the water, causing the growth of bacteria and algae, which will affect the cooling tower water flow rate and reduce the heat transfer efficiency; there are various salts in the cooling water, such as carbonates, bicarbonates, sulfates, silicates, phosphides, and chloride, etc. [37]. During the operation, the water is continuously concentrated due to the evaporation of water and scales during heat exchange with the equipment, which causes the pipe network to be blocked. In addition, there is no filtering device installed in the circulating water system, which cannot effectively remove these impurities, leading to an increase in the electrical conductivity of the water, causing corrosion of the pipeline, reducing the heat exchange efficiency [35], affecting industrial production in severe cases, and even paralyzing the entire system. In 2017, China promulgated the "code for design of industrial recirculating cooling water treatment" GB50050-95 [38], which stipulates the water quality standards for circulating cooling water, as shown in Table 2. The circulation system has a large drainage volume and high salt content. How to achieve low-cost and efficient desalination is the key to sewage reuse.

4. Circulating cooling sewage treatment technology

4.1. General circulating cooling sewage treatment technology

Traditional circulating cooling sewage treatment methods include scale inhibitor method and ion exchange method.

Table 1
Advantages and disadvantages of each adsorption material

Material	Advantage	Disadvantage
Activated carbon (AC)	Higher adsorption capacity, lower cost,	Smaller pore size and higher degree of pore bending
Carbon nanofiber (CNF)	Large specific surface area and good electrical conductivity	Slow diffusion in micropores and low capacitance
Carbon aerogel (CA)	High specific surface area, high density, high conductivity and controlled pore size distribution	Higher cost
Carbon nanotubes (CNTs)	High specific surface area, good electrical conductivity, and high stability,	Easy to aggregate, difficult to adsorb due to powder form
Graphene (GO)	High specific surface area, high electrical conductivity, and good chemical stability	Difficult to function independently
Metal-carbon material	High specific capacitance, good wettability and electrochemical performance	The preparation process is more complicated and the cost is higher

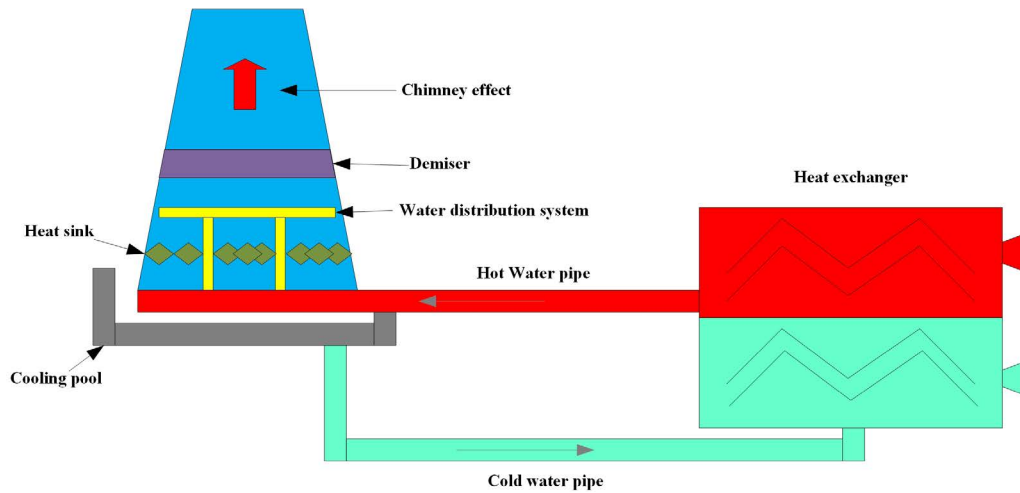


Fig. 7. Schematic diagram of circulating cooling system in power plant.

The scale inhibitor method can disperse the sparingly soluble inorganic salt in solution, and achieve the effect of preventing the insoluble inorganic salt from precipitating and scaling on the metal surface. Keep good heat transfer effect of metal equipment [39]. The ion exchange desalination method refers to the removal of cations (except hydrogen ions) in solution by using strongly acidic hydrogen type resins [40]. Although the ion exchange method has high effluent water quality, it needs to use a large amount of acid and alkali to regenerate and is inconvenient to operate, besides, it cannot work continuously and has serious environmental pollution. In addition, the use of acid–base regeneration resin is difficult to achieve the purpose of complete regeneration, especially for mixed-bed resin regeneration, so that the regeneration efficiency gradually decreases with the increase of resin use time. And the depletion of ion exchange capacity is unpredictable, which brings inconvenience to production, the circulating cooling sewage system usually needs to add chlorine to kill microorganisms in the solution. There are safety and secondary pollution problems in the production, transportation, and use of chlorine oxidants.

The representative of advanced processing technology is the membrane method, which mainly includes reverse osmosis, forward osmosis, high-pressure reverse osmosis, high-efficiency reverse osmosis, ultrafiltration-reverse osmosis, what is more, nanofiltration, and membrane distillation. Although the membrane desalination effect is remarkable, the problems of higher membrane cost and membrane fouling have not been effectively solved. For example, the double-membrane method does not take softening measures, and the hardness of wastewater is high, which makes the treatment of water quality unsatisfactory. The Langelier index of the sewage treated by the double-membrane method is too high, which is prone to scaling. If a large amount of descaling agent is used, it will increase the cost of sewage treatment. The use of “lime softening + ion exchange + RO” treatment process can greatly reduce the hardness of sewage, improve the operating efficiency of the reverse osmosis system, result in less waste of water resources and high system water recovery rate. However, in terms of design, the technology has complexity, especially the ion exchange technology needs to

occupy a large geographical area, the system has more stringent performance requirements, and a higher operating cost. The regeneration water of the exchanger is mostly acid solution, which has a great impact on the environment and affects the long-term stable operation of the equipment. In addition, the design of the microfiltration process is simple, which has the advantages of large cost and high efficiency. It can effectively remove organics and other chemical pollutants from the solution. In particular, the effect of treating iron ions in sewage is obvious. But the main difficulty is that the primary cost of unit water is too high, and further improvement is needed.

Emerging treatment methods for circulating cooling sewage include electrostatic water treatment, ozone treatment, magnetization treatment, and electro dialysis treatment. For example, Pan et al. [41] used electrostatic water treatment technology which had excellent processing effects, the algae removal rate reached 98% (scale), inhibition rate reached 95%, and sterilization rate reached 92%. The technology of electro dialysis desalination is mature and reliable, the equipment is modular and easy to manage, and the operating cost is only 1% of the ion exchange method. For medium to high salinity water quality (500–4,000 mg/L) [42]. Zhu et al. [43] conducted an experiment on the treatment of sewage from the circulating cooling system with an electro dialyzer technology. The results showed that the automatic operation mode of electrode switching could effectively solve the problems of concentration polarization and scaling of electro dialysis. When the water conductivity was 2,596–2,600 $\mu\text{S}/\text{cm}$, the best operating parameters of the electro dialyzer were: voltage 90 V, corresponding current 6.15 A, desalination rate 71.32%, and energy consumption 1.10 $\text{kW h}/\text{m}^3$. The produced water could meet the water quality requirements of the circulating cooling system. The disadvantages of electro dialysis technology are large energy consumption, low water production rate, and insufficient desalination efficiency. Due to the concentration polarization problem, electro dialysis is forced to operate at the limit current. However, in practice, the determination of the limit current density becomes more difficult as the operating conditions of the subject change, thereby limiting the effect of electro dialysis.

In brief, these methods have the problems of single removal of pollutants, huge equipment, high investment, and operation costs, and have been unable to effectively solve the problems of scaling and corrosion at the same time. In order to reduce sewage discharge, most of them are operated under high circulation rate conditions, and the consumption of antiscalants and bactericidal agents is also large. Therefore, in terms of technology selection, it is necessary to meet the needs of circulating water, reduce waste of resources, and promote the improvement of operating efficiency and meet the needs of modern society without energy. So it is urgent to find a new theory of circulating cooling and sewage treatment technology.

4.2. Application of CDI technology in circulating cooling wastewater treatment

It is an effective method to treat circulating cooling wastewater by CDI technology. The technology has been studied in the fields of seawater [44], municipal sewage [45], heavy metal-containing wastewater [46,47], dye wastewater [48], and phosphate wastewater [49]. In 2007, the first large-scale electrosorption sewage treatment plant in China was completed and put into operation in a water plant of a chemical company. The technology has the promotion value in the utilization of sewage resources in the chemical industry. After the electricity adsorption extracted the water back to meet the chemical production process water standard, it could be used as the process water, the boiler supplementary water and so on. The electrode adsorption device could reduce the suspended solids from 10 to 3 mg/L, the turbidity from 10 to 1 NTU, the ammonia nitrogen from 10 to 5 mg/L, and the COD_{Cr} from 25 to 10 mg/L. After the plant was put into production, it could reduce a large amount of pollutant emissions every year (including 9,022 tons of COD_{Cr} , 54,854 tons of BOD, and 1,560 tons of ammonia nitrogen), which can effectively improve regional water quality, and at the same time helped to alleviate the water supply pressure in cities with severe water shortage. After the treatment, the salt removal rate could reach more than 75%, the water recovery rate could reach more than 75%, the electricity consumption was 1 kW h/m³, and the water production cost was low, and the cost of quality recycled water per ton was 1.95 Chinese Yuan. The process was unique in China and internationally advanced. It had the characteristics of simple pretreatment, low power consumption and low operating cost, long service life of equipment, simple operation management, and wide application range. The application of CDI technology in petroleum, chemical, metallurgical, and other fields have been relatively mature, but it is still at preliminary stage in the treatment of circulating cooling and sewage.

Liu et al. [50] used polypyrrole/polyacrylonitrile-based carbon fiber (PPy/PCF) as the electrosorption electrode in this study, which was used to treat the simulated power plant circulating cooling sewage. The results showed that the PPy/PCF composite electrode could ensure the desalination efficiency of brine when the inlet COD was greater than 300 mg/L, and had the advantages of reducing cost and simplifying pretreatment device. Ma et al. [51] studied the desalination performance and main ion removal effect under the optimal experimental conditions by taking the actual

circulating cooling effluent as the research object. The results showed that the maximum salt removal rate was 75.63% and the average salt removal rate was 60.66%. The average removal rate of Ca^{2+} was 50.1%, the average removal rate of Mg^{2+} was 48.5%, the average removal rate of sulfate was 51.21%, and the average removal rate of Cl^- was 69.99%. The experimental data effectively showed that the CDI technology has a good treatment effect in the desalination treatment of circulating cooling sewage in power plants. Liu et al. [52] used CDI desalination technology to demineralize the circulating cooling sewage, and treated the water quality (salt, chloride, total alkalinity, total hardness, turbidity, and other indicators) for analysis, focusing on the de-salting effect and influencing factors of circulating water. The test results showed that the CDI desalination device can effectively remove the ions in the circulating cooling sewage of the power plant, and the conductivity, total hardness, alkalinity, chloride, and turbidity of the produced water can meet the reuse requirements. Shen et al. [53] applied the CDI technology to the field of wastewater desalination and reuse, and carried out experimental research and analysis in order to solve the problem of high salt content, large water production and difficult reuse of the circulating water system of the power plant. The results showed that hardness and Cl^- removal rate could reach over 65%, and some COD could be removed. The cost was about 0.5 Chinese Yuan per ton. The whole CDI test device could achieve continuous and stable operation, and it showed good feasibility for the primary desalination treatment of circulating wastewater in power plants. Li et al. [54] conducted a preliminary study on the desalination effect of sewage discharged in the circulating cooling sewage system by using CDI desalination technology. The experiment showed that the average desalination rate and water production rate of electrode adsorption technology were 76.3% and 76.1%, respectively. The average energy consumption per ton of water was 1.33 kW h. The water quality of the produced water could meet the requirements of the supplementary water in the circulating cooling sewage system.

A purification equipment company uses the CDI process to treat the circulating cooling sewage of the power plant. The process is divided into three steps: work process, regeneration process, and sewage discharge process:

- *Work process*: the original water is fed into the pretreatment unit through the water pump to remove any suspended solid or sediment more than 5 μm . After that, the dissolved salts in the circulating cooling water are adsorbed and the water quality is purified.
- *Regeneration process*: it is the backwashing process of the electrode plate, flushing the module through short-circuiting with raw water to regenerate the electrode. The backwashed water is sent to the intermediate pool, and the water entering the middle pool is waiting for the next cycle of sewage.
- *Sewage process*: the essence of the sewage discharge process is the same as the regeneration which is a backwashing procedure of the module, but the water source is different. The sewage process uses the water in the middle pool to increase the water production rate. The average conductivity of raw water is 4,176 $\mu\text{S}/\text{cm}$, the average conductivity of water production is 859 $\mu\text{S}/\text{cm}$, and the average removal rate of conductivity is 79.43%:

Table 2
Design specifications for industrial circulating cooling water treatment

	Requirements and conditions of use	Allowance range
Suspended matter, mg/L	Determined according to production process requirements	≤ 20
	Heat exchange equipment is plate type, rocker tube type, spiral plate type	≤ 10
pH	Determined according to the formulation of the medication;	7.0–9.2
Methyl orange alkalinity, mg/L	Determined according to pharmaceutical formula and working conditions	≤ 500
Ca ²⁺ , mg/L	Determined according to pharmaceutical formula and working conditions	30–200
Fe ³⁺ , mg/L	–	<0.5
Cl ⁻ , mg/L	Carbon steel heat exchange equipment	$\leq 1,000$
	Non-carbon steel heat exchange equipment	≤ 300
SO ₄ ²⁻ , mg/L	Sum of [SO ₄ ²⁻] and [Cl ⁻]	$\leq 1,500$
Silicic acid, mg/L	–	≤ 175
	Product of [Mg ²⁺] and [SiO ₂];	<15,000
Free chlorine, mg/L	–	0.5–1.0
Oil, mg/L	–	<5
	Oil refinery	<10

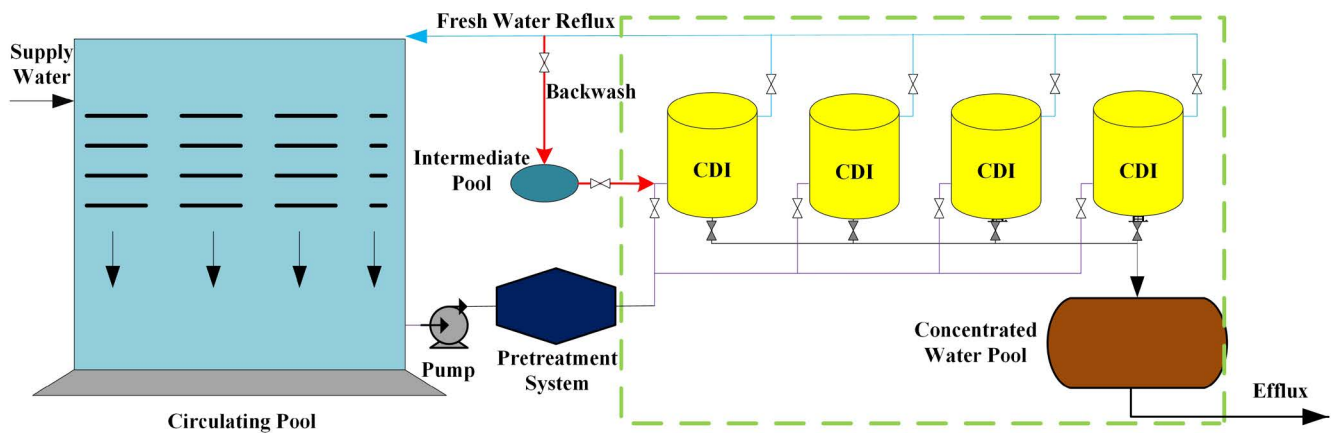


Fig. 8. Schematic diagram of CDI for circulating cooling and sewage treatment.

the average concentration of raw water chloride is 712 mg/L, the average yield of water is 91 mg/L, and the average removal rate reaches 87.22%; the average hardness of the raw water is 19.88 mmol/L, the average hardness of the produced water is 5.66 mmol/L, the removal rate is 71.53%, the original average sulfate is 990 mg/L, the average value of the sulfate produced by the water is 190 mg/L, and the removal rate reaches 80.81%. Fig. 8 is a schematic view showing the treatment of CDI for circulating cooling sewage.

In summary, the CDI technology has a good removal effect in the treatment of circulating cooling sewage. Compared with the traditional water treatment and desalination

technology, CDI technology has the following advantages for circulating cooling sewage treatment:

- *Large amount of adsorption*

The selected adsorbent material has a large specific surface area namely has a good adsorption capacity. After electrification, the adsorbent material will form a double electric layer on the surface, and the diffusion layer of the double electric layer will be compressed, which will increase the charge density and the demand for anti-ions, so that more ions will be concentrated into the EDL. Under the action of the electric field force, the ion migration rate also increases, which makes it easier for ions to be adsorbed on the material.

Table 3
Table of energy consumption ranges for various water treatment technologies

Technology	The range of required energy consumption (KW h/m ³)
MSF	10–58
MED	6–58
RO	2–6
ED	0.4–8.7
CDI	0.1–2.03

Further, the adsorbed material after the energization is 5–10 times larger than the adsorption capacity of the unenergized adsorbent.

- *Lower cost*

The investment in the electrosorption process unit is slightly higher than that in the thermal and membrane process units, but in the subsequent operation, the cost of dosing and membrane replacement are reduced. Since the adsorbent material is generally selected from a cheap and readily available carbon material, it has good stability and does not need to be replaced frequently. Moreover, the CDI device operates at low pressure and requires low energy consumption, so that the water production cost is low. Table 3 shows the energy consumption range of each water treatment technology [55].

- *No need to add chemicals*

Without adding any chemicals, the salt in the water can be removed, saving costs, and avoiding secondary pollution.

- *High degree of automation*

The process flow is simple, unattended, and the technical requirements of the operator are low.

- *Clean and pollution free*

The components contained in the concentrated water are derived from raw water, and the system itself does not produce new emissions, avoiding secondary pollution.

- *Flexible operation*

The switching between the adsorption and desorption processes can be achieved by just doing reverse polarity operation, with high flexibility.

4.3. Future development trend of CDI technology

CDI technology is a new type of water treatment technology, and it has many advantages. But the research and application of this technology are not widespread application at present, it still needs to be improved, as shown below:

- Firstly, the efficiency of mass transfer of the CDI system needs to be improved. In order to solve this problem, it should focus on the development and research of electrolytes and electrode materials to reduce energy consumption. At the same time, the electrode stability and irreversible Faraday reactions should be considered during the experiments [56]. For example, carbon electrode oxidation and oxygen reduction cause the formation of chemical byproducts and pH fluctuations of the product water, reducing salt-water separation and increasing energy consumption over time [57–59]. In addition, membrane fouling, and scaling of electrodes are also major issues that cannot be ignored [60]. It should also be noted that the natural organic matter (NOM) is abundant in natural waters, which can be adsorbed onto the electrode surface to the number of available sites for salt adsorption [61].
- In the future development of CDI technology, the design of CDI reactor is also an important development direction. It is possible to design a reactor with special structure by increasing the specific electrode area, mass transfer efficiency, and water yield, so as to optimize the shortcomings of traditional technology. For example, flow-by CDI stands out owing to its simple structure without the need of expensive ion exchange membrane or pumping energy requirements for flow-electrodes. MCDI presents higher charge efficiency than flow-by CDI at the cost of significantly more expensive cell components [17]. CDI cells with battery electrodes (HCDI, desalination battery and CID) regularly achieve salt adsorption capacity far exceeding that of CDI cells with capacitive electrodes. However, battery electrodes exhibit a slower salt removal and incur a higher capital cost relative to capacitive electrodes [62].
- CDI water treatment technology cannot complete the simultaneous removal of some pollutants in current situation, so it is necessary to integrate it with other water treatment units. For example, the combination of the traditional seawater desalination process with the CDI treatment system can effectively extend the working life of the membrane and reduce the cost, and give full play to the advantages of their respective technologies.

5. Summary and outlook

As a potential water treatment technology, CDI has attracted wide attention due to its low energy consumption, high efficiency in salt removal, and pollution-free. Although CDI technology has made progress in many water treatment fields, it is still in its infancy in the treatment of circulating cooling sewage treatment. Due to the slightly higher investment costs and restrictions on salt content, industrial applications have not been realized.

The circulating cooling sewage contains a large amount of calcium and magnesium ions, which will form a poorly soluble substance with the hydroxyl group generated by the CDI reaction, resulting in a decrease in the reaction capacity of the CDI system. Therefore, it is necessary to solve the problem of efficiently removing the hardness ions and alleviating the surface contamination of the electrolyte. In addition, low energy utilization efficiency, small water treatment

flux, and poor operation stability are the weaknesses of the CDI system. How to realize the high-flux operation of the electrosorption reactor is another difficulty to be solved, among which the optimal design of the reactor and electrode materials are the solutions. Believe that as technology advances, these problems are expected to be resolved. In general, CDI technology has a large development space in the field of desalination, especially in the reuse of water resources, which has a broad application prospect.

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