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The Expanded Electrodeionization Method for Sewage Reclamation

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Additional information is available at the end of the chapter

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Abstract

The aim of the chapter is to introduce a new technology using the flow-divided electrodes for sewage reclamation based on redox and concentrating ions. This creative system can be used directly for sewage treatment without the need for costly ion-exchange membranes and other chemical reagents. Under experimental conditions, the removal percentage of TDS (total dissolved salts) is 83 % and the removal percentage of COD (chemical oxygen demand) is 92 %.

Keywords: Flow-divided electrodes, expanded electrodeionization, sewage reclamation, ion-exchange

1. Introduction

In general, urban sewage discharge accounts for 75_85% of the consumption and the industrial sewage discharge accounts for 80_90% of its consumption. Sewage, that is actually utilized in a biological or chemical way and disappears in the form of vaporization loss is less than 25%. Because of the low rate of sewage treatment in China, the majority of the surface water resources and the underground water resources are polluted to different extents, resulting in extra pressure, caused by the shortage of water resource, on the sound and sustainable development of economy and society. Sewage reclamation is not only favorable for enterprises to increase income and decrease expenditure as well as reduce consumption and improve efficiency, but is also an inevitable option for enhancing the supply capacity of urban water.

It is more important to improve the revitalization environment of aquatic ecosystems, benefiting not only the present generation, but also future generations. Advanced sewage treatment means that, in order to cause urban sewage or industrial wastewater, which has been subjected to routine treatment, to reach a certain standard of recycled water and to be reused for production or living, treatment units are added in order to further remove the pollutants that cannot be removed by routine treatment, such as heavy metals, COD (chemical oxygen demand), TN (total nitrogen), TP (total phosphorus), TDS (total dissolved salt) and the like.

The electrochemical process has the prominent characteristics of wide adaptability, good cleaning property and easy control in removing the pollutants in sewage water, and its course is mainly mass transfer control. Firstly, it is necessary to eliminate the ohmic resistance between electrodes with a supporting electrolyte such as sodium chloride. However, the wide application of this method is limited by water recycling. Secondly, the reaction products (especially gases such as hydrogen from cathode and oxygen and carbon dioxide from anode as shown in Figs.1 and 2) inhibit the reactants at the reaction zone and increase the ohmic resistance markedly. Thirdly, the scaling on cathode accumulates over the reaction zone and decreases current efficiency.

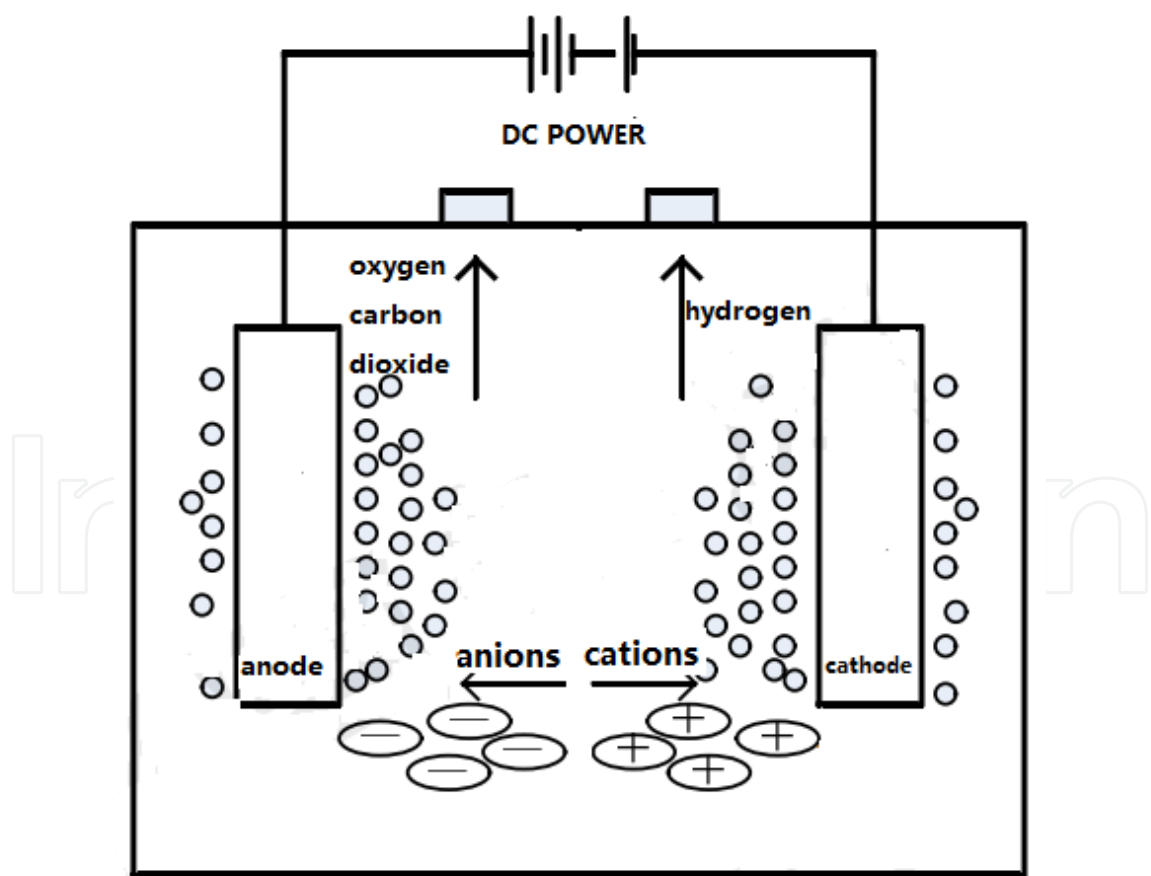


Figure 1. A schematic illustration of a sewage electrolysis system

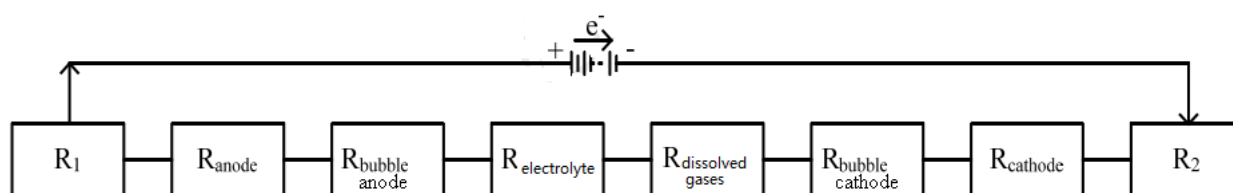


Figure 2. Electrical circuit analogy of resistances in a sewage electrolysis system

As shown in Fig.2, electrochemical resistance consists of the electrical resistance (R_1 R_2) reaction resistance (R_{anode} R_{cathode}) and transfer resistance ($R_{\text{anode bubble}}$ $R_{\text{electrolyte}}$ $R_{\text{dissolved gases}}$ $R_{\text{cathode bubble}}$). Transfer resistance in a sewage electrolysis system is negatively related to the reaction resistance. Decreasing energy consumption of the electrochemical process is a challenge.

Combination of ion exchange and electrochemical technology research from the beginning that the ion exchange membrane i.e. the electrodialysis technology. Ion exchangers and selective ion exchange membranes having ion conduction capability are simultaneously used in, electrodeionization (EDI) and to overcome the defects that electrolyte addition causes in the process of electrolytic reaction and chemical regeneration in the process of ion exchange. However, the particularity of hydrogen ion and hydroxyl ions (migration behavior in the electric field and selectivity of hydrogen ion to strongly acidic cation exchange resin and hydroxyl ions to strongly basic anion exchange resin) limits the efficiency of the electrical energy. Polarization caused by the verticality of membrane surface and flow field to electric field, as well as their impacts still exist as key factors that restrict the improvement of operation efficiency and the widening of applicable scope, their practical applications still require improvement.

The aim of this chapter is to provide a new technology using flow-divided electrodes for sewage reclamation based on redox and concentrating ions. This creative system can be used directly for sewage treatment without use of costly ion-exchange membranes and other chemical reagents. Under experimental conditions, the removal percentage of TDS (total dissolved salts) is 83 % and the removal percentage of COD (chemical oxygen demand) is 92 %.

2. Technological process

Fig 3 is a schematic diagram of the super advanced sewage treatment process. We proposed a novel EEDI system by introducing porous flow-divided electrodes (FDE) as the electroosmotic unit. During operation process, the flow of wastewater and gases from electrodes is controlled so as to penetrate into the internal part of FDE, which we call as the flow-divided model (Fig 3). The flow field is parallel to the electric by means of the porous FDE, thus avoiding mutual interference between the cathode reaction and the anode reaction, and reducing the ohmic resistance and mass transfer resistance ($R_{\text{anode bubble}}$ $R_{\text{cathode bubble}}$), and realizing separation of the anolyte (containing oxygen and carbon dioxide) and catholyte (containing hydrogen) without any diaphragm (Fig 4).

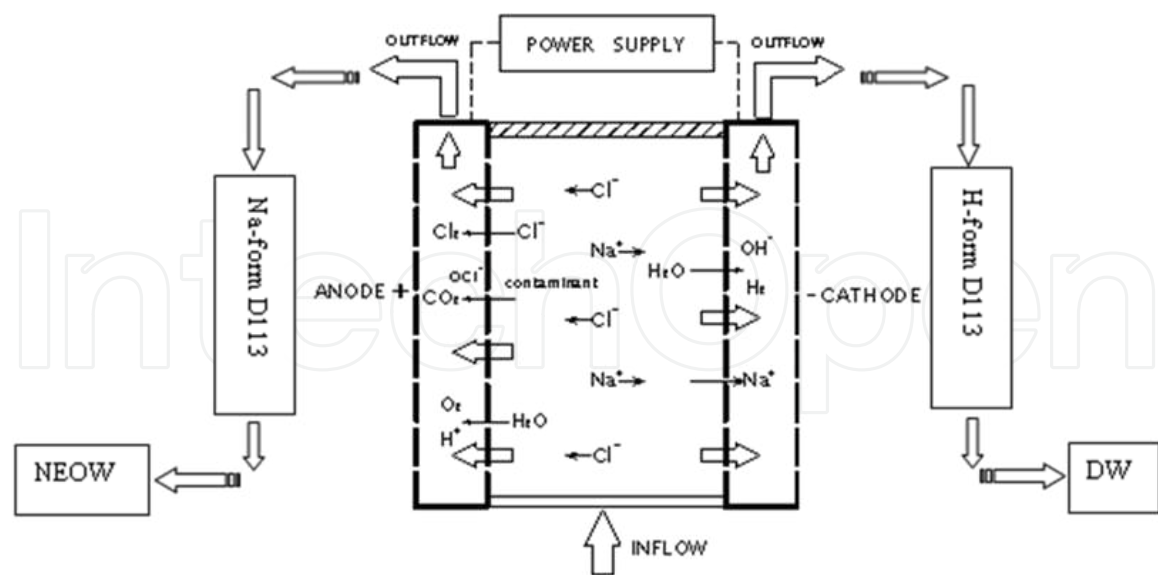


Figure 3. Schematic diagram of the Super Advanced Sewage Treatment process

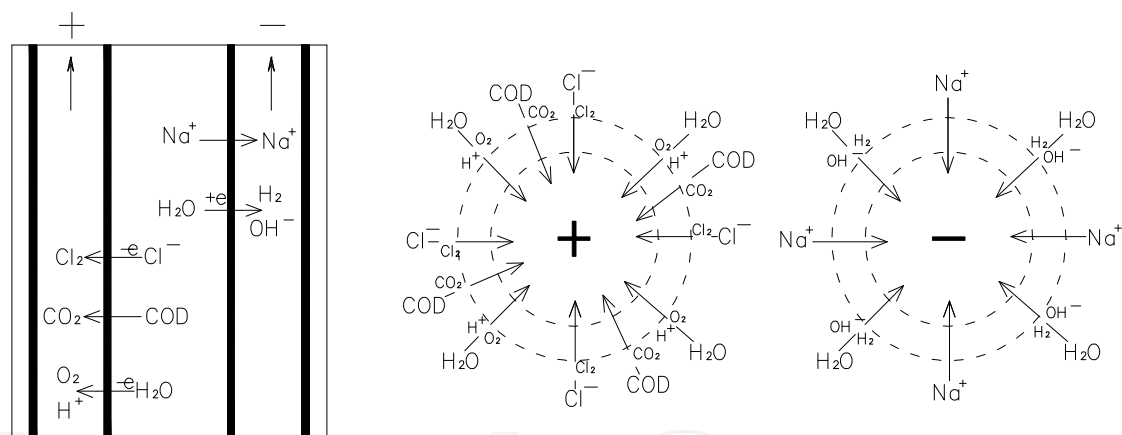


Figure 4. Mechanisms of ion migration to the electroosmotic section

Furthermore, polarity of the electrodes can be flexibly switched, thus eliminating cathode scaling during extended operation. The EEDI utilizes electrochemical redox and ion-exchange simultaneously to produce the concentrated electrolyzed oxidizing water (EOW), desalted water (DW) and hydrogen as by-product.

Since the anodes and cathodes in the EEDI are completely uniform and no ion-exchange membranes are used, it can be operated by switching anodes and cathodes flexibly for eliminating the scaling on the surface of cathodes. The strongly basic anion exchange resin grains placed among the anode and cathode act as supporting electrolyte, enabling the treatment of wastewater with low salt. The concentrated and neutralized anolyte containing active chlorine is effective for disinfection and contaminant removal.

3. Materials and methods

3.1. Titanic porous FDE and electroosmotic unit

The electroosmotic unit was constructed with three hexagonal anodes and cathodes (area 0.0113 m²) within a insulated polymethyl methacrylate shell(Fig 5). The distance of between anode and cathode is 25 mm and they are packed with strong basic anion exchange resin grains (201×7, properties shown in Table 2). The electrolyzed oxidizing water (containing gases) and electrolyzed reducing water were pressed to flow out of the anode and cathode, respectively (see Fig 3).

	Dimension (mm)	Porous dimension (μm)	Porosity factor (%)	Penetrability of gas (L/cm ² minPa)	Compression resistance (Mpa)	Most pressure difference (Mpa)
value	Φ12×100	30-50	28-50	0.02-20	0.5-1.5	0.6

Table 1. Properties of the porous FDE

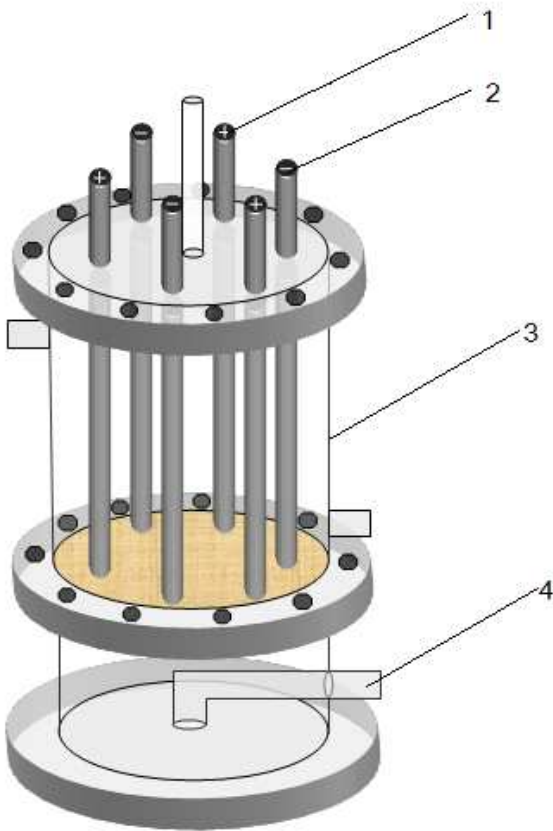


Figure 5. a structural schematic diagram of the electro-osmotic unit 1—anode, 2—cathode, 3—organic glass shell, 4—sewage inlet.

Group	Exchange capacity (mmol/ml)	Diameter (mm)	Water content (%)	Density (g/ml)	Upper limit		
					Expansibility (%)	temperature (°C)	pH range
-N ⁺ (CH ₃) ₃	≥1.4	0.6_1.4	42_48	1.06_1.11	Cl → OH:18_22	100	1_14

Table 2. Properties of 201×7type strong basicity anion exchange resin

3.2. Ion exchange treatment and regeneration

The electrolyzed oxidizing water out of anode was pumped into Na-form D113 column (regeneration), whose properties are shown in Table 3. The electrolyzed reducing water out of cathode was pumped into H-form D113 column (treatment).

Group	Exchange capacity (mmol/ml)	Diameter (mm)	Water content (%)	Density (g/ml)	Expansibility (%)	Upper limit	
						temperature (°C)	pH range
-COO ⁻	≥10	0.35_0.55	45_52	1.15_1.20	(H → Ca) 20_30	100	5_14

Table 3. Properties of D113 weak acid cation exchanger

3.3. Sewage treatment

The flux of the simulated wastewater (properties shown in Table 4) is 7.5 L/h. The voltage of the electroosmotic unit is controlled at 25 V. The ratio of electrolyzed oxidizing water and electrolyzed reducing water is 1. The COD was determined by bichromate method. Concentration of Cl⁻ was determined by titration with silver nitrate solution. A power supply (LW10J10) was used to maintain constant DC voltage. Conductivities were measured by a conductometer (DDS-IIA). The pH of water was measured by an acidimeter (DELTA320). Temperature was held at room temperature during all experiments.

3.4. Cooling water treatment

The flux of the cooling water (properties shown in Table 5) is 3.0L/h. The voltage of the electroosmotic unit is controlled at 15 V. The ratio of electrolyzed oxidizing water and electrolyzed reducing water is 0.5. Apparent current density was between 88 and 90 Am⁻².

4. Results and discussion

4.1. Treatment of the simulated wastewater

The properties of water samples, including the feed, electrolyzed oxidizing water, electrolyzed reducing water and the desalted water are shown in Table 4. The removal percentage of TDS and the removal percentage of COD for the desalted water are 83 % and 92 %, respectively.

This result demonstrates that the novel flow-divided EEDI can remove contaminants effectively without chemical reagents.

	Cl ⁻ concentration (mg/L)	pH	Conductance(μs/cm)	COD(mg/L)
Simulated wastewater	689	7.28	2100	426
Electrolyzed oxidizing water	2899.10	2.24	---	---
Electrolyzed reducing water	120.00	12.36	4500	---
Desalted water		4.16	350	32.6

Table 4. Properties of the feed and the electrolyzed oxidizing and electrolyzed reducing water

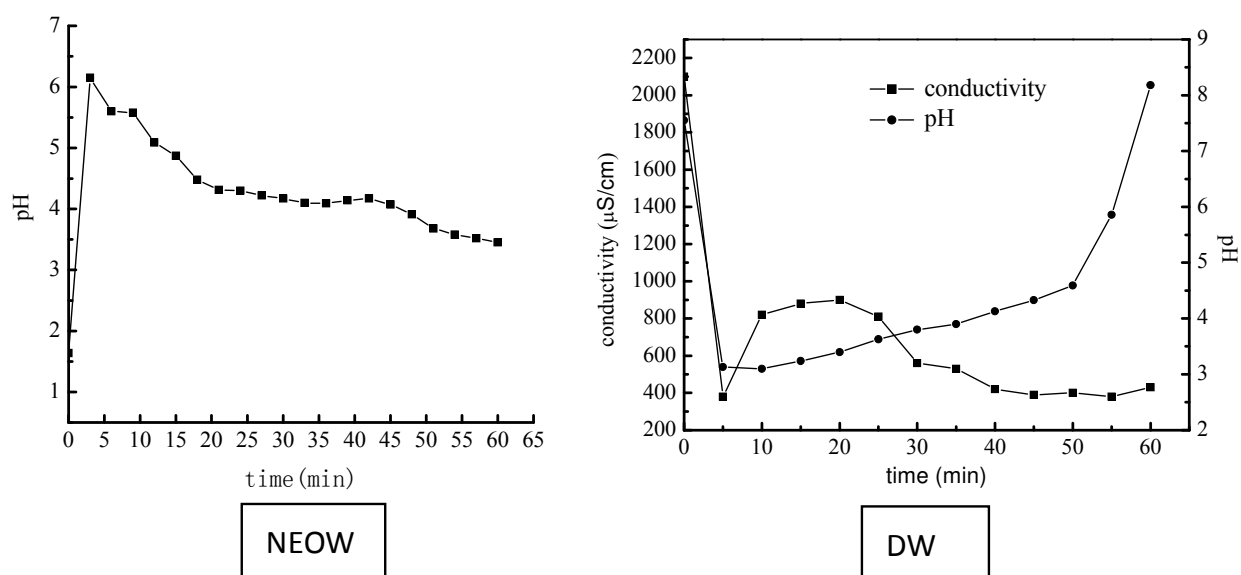


Figure 6. The pH of NEOW and DW versus time

Fig 6 shows pH variation for EOW and DW from flow-divided EEDI versus time. It can be seen that pH of EOW gradually decreased, while pH of DW gradually increased with time. The change of pH can periodically provide information about the transforming degree of the ion exchanger for the polarity reversal operation.

4.2. Mechanism of ion migration and COD removal

The strong base anion exchange resins placed between anode and cathode play an important role in gathering anions, in adjusting ion migration and acting as the supporting electrolyte. There are three routes for anion migration: (1) ions migrate alternatively through solution or ion-exchange resins, (2) ions migrate through ion-exchange resin grains and (3) ions migrate in solution. However, there is only one route for cation migration, that is, through solution (Fig 7). Furthermore, the diffusion coefficient for ion migration in ion-exchange resins is much

higher than that in solution. As a result, the amount of anions in anode affinity is much higher than the cations in cathode affinity. Chlorine ions thus gathered in anode around and formed concentrated chlorine water. The relevant reactions are shown as follows:



The organic substances (or HCO_3^-) around the anode are oxidized directly or indirectly into carbon dioxide or intermediates. The hydroxide ions are concentrated and passed through the filter cylinder cathode. Hydrogen formed by water electrolysis penetrates into the inner part of FDE by the force of electric fields and flow fields. In this case, concentration and ohm resistance can be reduced remarkably. Hydrogen evolution from water electrolysis is shown as follows:

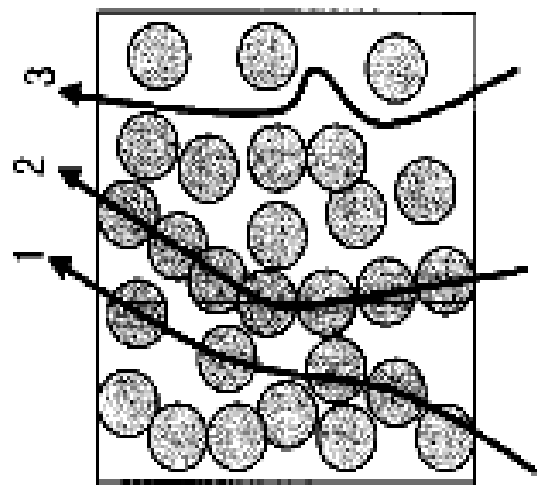


Figure 7. Schematic representation of the three paths that the current can take

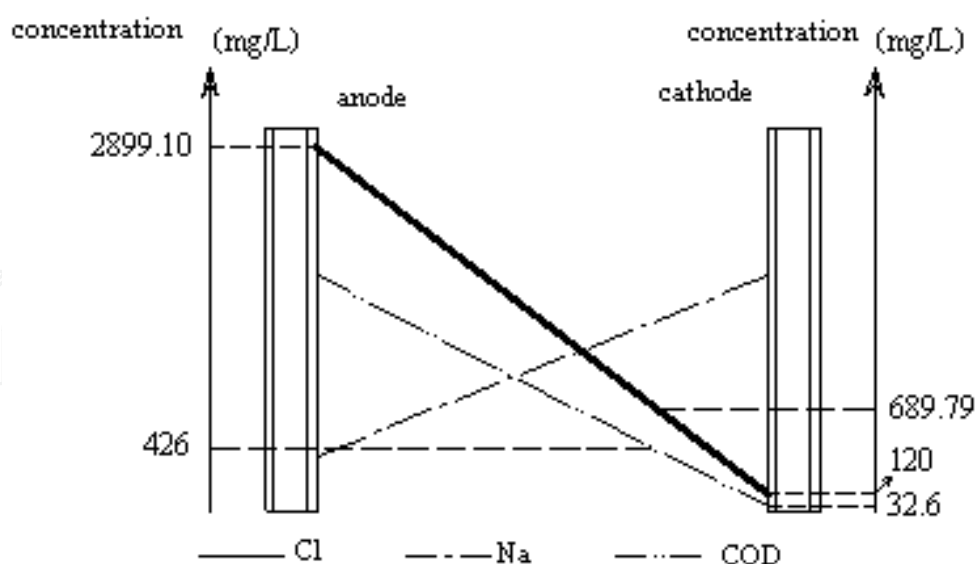
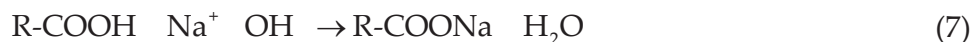


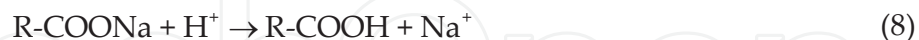
Figure 8. Distribution of the species between anode and cathode

4.3. Reaction of ion exchange

The neutralization reaction between the electrolyzed reducing water and the H-form D113 resin is as follows:



Na^+ Ions are adsorbed on ion-exchange resin, thereby desalting the feeds. The Na-form D113 ion-exchange resin was regenerated into H-form D113 with electrolyzed oxidizing water for reuse. The reaction is shown as follows:



Since the cathodes and anodes in EEDI are completely uniform and no ion-exchange membrane are used in this system, this flow-divided EEDI can be operated by switching anodes and cathodes flexibly, eliminating the scaling on the surface of cathodes.

4.4. Mass balance

The mass balance of this novel flow-divided EEDI was calculated according to the ratio of electrolyzed oxidizing water and electrolyzed reducing water as shown in Fig 5. As mentioned in Section 3.2, NaCl was concentrated in anode around up to 83 %(mass ratio) with the help of strong base ion-exchange resin. Organic contaminants were oxidized in anode with COD removal percentage of 92 %.

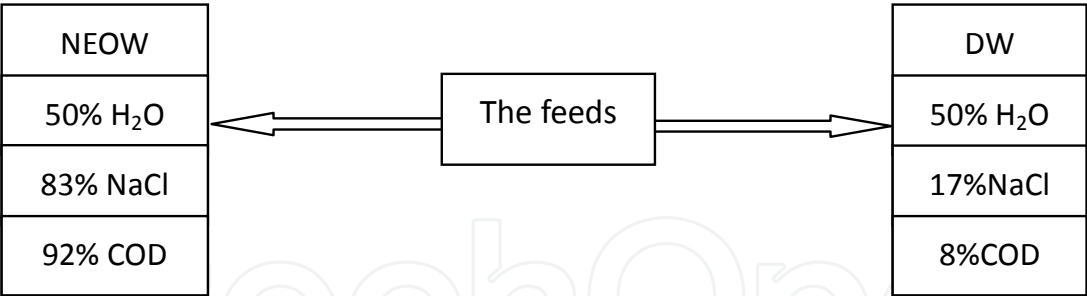


Figure 9. Schematic representation of mass balance

4.5. Treatment of the cooling water

4.5.1. Material equilibrium of the cooling water treatment

The properties of the cooling water and the desalted water are shown in Table 5. The removal percentage of the hardness and the removal percentage of Cl⁻ for the desalted water are 98 %and 74 %, respectively. The removal percentage of dissolved oxygen is 36 %.

	Conductance (μ s/cm)	DO (mg/L)	pH	Cl ⁻ (mg/L)	Hardness (CaCO ₃ mg/L)
Cooling water	2100	7.5	7.55	479.85	750
Desalted water (DW)	580	4.6	6.57	189.94	30

Table 5. Properties of the feed and the desalted water

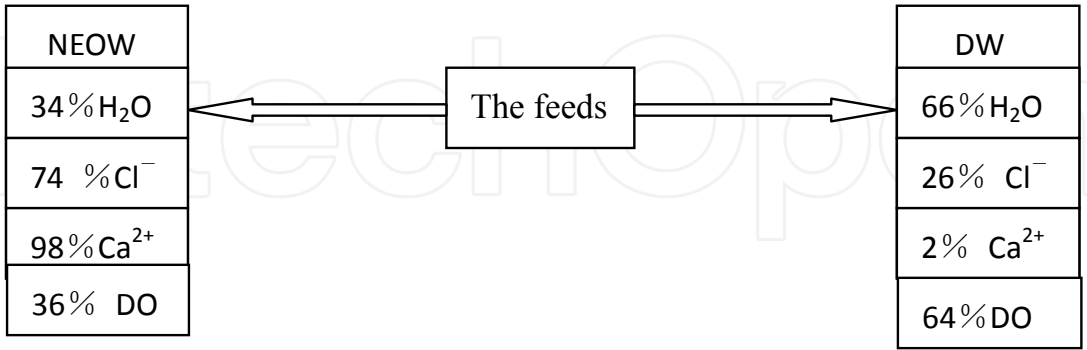


Figure 10. Mass balance of the cooling water treatment

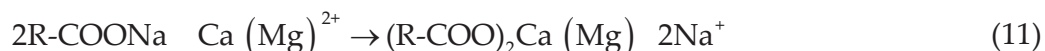
4.5.2. Mechanism of DO and hardness ions removal

The water passes through the cathode and the following reactions take place:



The above reaction decreases the dissolved oxygen content of the cooling water and contributes to corrosion control in the circulating system.

The electrolyzed reducing water with the higher pH goes into the series type hydrogen D113. Neutralization and exchange reaction is shown as follows:



4.5.3. The sterilization effect

Fig 11 shows bacterial concentration in the feed and DW samples. It can be observed that there are groups of bacteria in the feed sample. When water passes through the electrode, the bacteria are destroyed by directly touching the electrodes. As a result, no bacteria exist in the culture dish. The DW does not come in contact with the active chlorine, but the bacteria are destroyed by cathode and electric field.

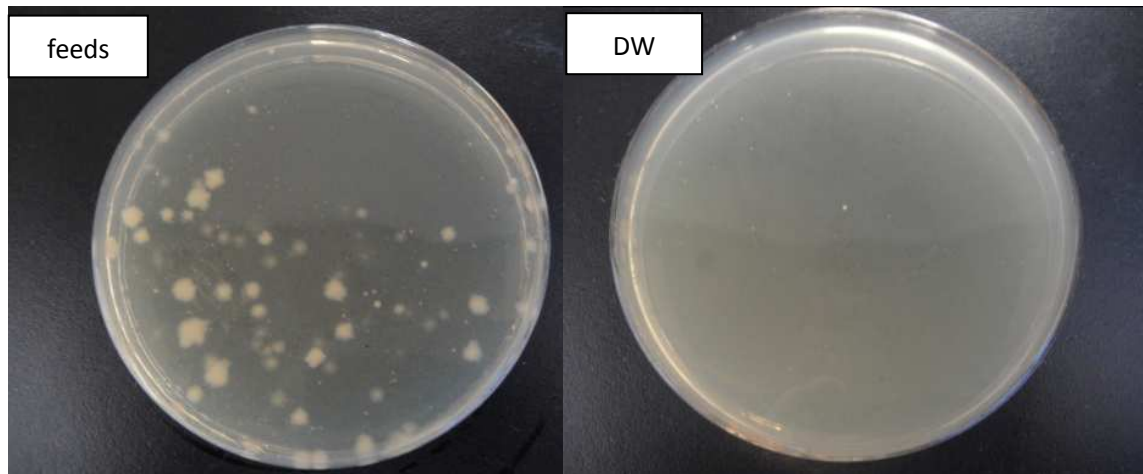


Figure 11. Comparison of bacterial concentration in the feed and the DW

5. Conclusion and expectation

The electro-osmosis ion exchange method presented here has wide adaptability in the aspect of the super advanced purification of sewage, no chemical agent is needed and no secondary pollution is caused.

The electro-osmosis unit does not require the use of membranes, the cathode/anode-equivalent micropore titanium filter electrode array and the design adopted, such that the flow field is parallel to the electric field, avoids mutual interference between the cathode reaction and the anode reaction and reduces current reduction and mass transfer hindrance, which are caused by gas coverage generated in the process of electrolysis. Furthermore, the elimination of scaling of electrodes through electrode reverse operation and the regeneration and continuous operation of subsequent ion exchange resin are facilitated.

Filling resin between the electrodes results in an electrolyte supporting effect, so as to avoid the limitation on the electrical conductivity of influent. Electrolyte addition is not required when sewage with low electrical conductivity is treated.

The invention provides a new way for pollution control and resource recycling, has become an extremely promising technology as the recycling of H_2 is turned into another point for economic growth and will bring wide prospect to ion exchange application technology in the field of sewage reclamation.

A wide space is provided for the application and development of the electro-osmosis ion exchange method due to diversified commercial ion exchangers.

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