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Alkaline salt solution resin for inorganic salt wastewater treatment

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ABSTRACT

For developing countries, the progress of urbanization will bring certain water pollution problems, and the treatment of industrial wastewater is more difficult. Aiming at the treatment of inorganic salt industrial wastewater containing chloride ions, a kind of strong alkali type anionic resin with bicarbonate radical free group and weak acid type cationic resin with large pore based on sodium bicarbonate solution is designed. A set of chloride ion inorganic salt purification method based on this material is designed. The laboratory findings denote that the maximum time of the improved salt solution resin, reverse osmosis membrane method and multi-stage contact oxidation process in the pH range of 6.5~8.5 is 150, 120 and 110 min, respectively. When the chloride ion concentration of the original wastewater is greater than 0.04 mol/L, the qualified rate of the effluent by the designed method is higher than that of all the compared processes. When the unit bed is less than 80, the average chloride ion concentration of the designed method, reverse osmosis membrane method and multi-stage contact oxidation are 47, 92 and 78 mg/L, respectively. From the experimental data that the process of alkaline salt solution resin designed based on this study is stronger than the commonly used methods in the market in terms of chloride ion inorganic salt purification capacity of wastewater, and the water purification capacity is longer.

Keywords: Inorganic salt wastewater; Chloride ion; Alkaline salt solution; Sodium bicarbonate

1. Introduction

Inorganic salt wastewater (ISW) refers to the wastewater containing inorganic salt chemical substances, which often appears in industries such as electroplating and fertilizer. As the rapid growth of these industries, more ISW is discharged in some cities, which makes the treatment and recycling of these wastewater more prominent [1]. Traditional ISW treatment methods mainly include biological, physicochemical, membrane separation, evaporation methods and so on. These methods are effective, but each has some problems. For example, biological treatment has low efficiency, long treatment cycle and is susceptible to environmental interference; Membrane separation is costly and prone to technical bottlenecks [2,3]. Therefore, how to find a new method for the disposal of ISW is one of the hot spots in the current research field. This study will discuss the treatment method of ISW with alkaline inorganic salt as the mixing agent. Resins are also used in wastewater purification materials. Resin is a kind of polymer compound with excellent adsorption properties and selectivity. By adsorption and desorption of resin, plasma separation and recovery of lithium, strontium, sodium, magnesium and ammonium in ISW can be realized. The purpose of low-cost wastewater treatment and inorganic salt recovery is realized.

This research will be elaborated from the following aspects: Firstly, the background and development status of ISW industry are introduced; Secondly, the present technical

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routes and advantages and disadvantages of ISW disposal are introduced in detail. Finally, based on the related basic concepts and from the perspective of resin, the ISW treatment method mixed with bicarbonate salt and resin is studied, and the performance and application value of this method are analyzed by designing experiments.

2. Related works

The treatment of ISW is of great significance for improving the quality of urban water resources and urban ecological environment. Rajagopalan et al. [4] found that a large amount of ISW was generated during the production of phase change materials used for thermal energy storage. Therefore, the author designed a process for the purification of phase change materials production wastewater based on inorganic salt polymer solution and gel. The experimental findings indicate that the treatment effect of this material on ISW in the production of phase change materials was better than that of traditional wastewater purification methods. Ghimici and Constantin [5] found that polymeric derivatives based on polysaccharides were receiving increasing attention due to their availability and environmental protection. However, although pullulan is a polysaccharide with high solubility and flexible skeleton, there are still huge research gaps in its application in wastewater purification. In this study, it summarized the flocculation and adsorption properties of some pullulan derivatives that have been evaluated in wastewater containing inorganic salts or organic pollutants. Studies have shown that parameters such as contaminants, polymer type and environmental characteristics could affect the purification efficiency of this pullulan derivative. The accumulated knowledge provided a reliable basis for the application of pullulan derivatives in wastewater purification. Vesely et al. [6] have devised a way to treat ISW using layered black phosphorus to prepare metal nanoparticles. Layered black phosphorus is a kind of anisotropic and interlayer gap dependent layered material, which can be stripped to single layer phosphide. Compared with graphene, fewer layers of black phosphorus and its single layer phosphide had higher reactivity and could be used to self-catalyze the reduction of gold ions into gold nanoparticles supported on fewer layers of black phosphorus. Both black phosphorus and gold were important oxidation catalysts, which played an important role in the catalytic treatment and purification of organic synthesis and industrial wastewater. The results denoted that gold nanoparticles have a good effect on the treatment of ISW in the process of wet oxidation of phthalate. In addition, the gold nanoparticle catalyst had a high stability in the purification capacity of ISW, which provided a new idea for the treatment of ISW. Wang et al. [7] found that domestic solar driven interface evaporation technology still had some problems in the treatment of dye wastewater that have not been well solved, such as reducing the evaporation rate when treating high-concentration dye wastewater containing inorganic salts. Therefore, a ceramic solar steam generation filter was designed, which can treat dye wastewater containing inorganic salts efficiently. The research outcomes expressed that the solar steam generation filter had good pH stability, thermal stability and strong mechanical properties, which could meet the practical application requirements in complex environments, and had excellent inorganic salt purification capacity. Cui et al. [8] designed a novel acid-resistant composite semi-permeable membrane prepared by interfacial polymerization, in which the aqueous phase was a solution of mixed phenylenediamine and triethylene tetramine, and the organic phase was a solution of 1,3-phenyldisulfonyl chloride. The acid resistance of the composite film was evaluated by total reflection Fourier-transform infrared spectrometer, energy dispersion spectrometer and weight loss test. The results denoted that the water flux of the membrane was stable when it treated 3.5% NaCl solution. After soaking in 20% sulfuric acid solution for a week, the salt retention rate did not decrease. This acid-resistant organic molecular membrane had certain potential application value in the treatment of ISW. Zhang et al. [9] investigated the effect of trioctylamine (TOA) as an extractant in sulfonated kerosene to extract chloride from wastewater. The optimal operating conditions were determined by univariate experiment. The chloride removal rate of the material was 79.11%, which was higher than that of the traditional extraction method. This study provided new ideas for the removal of inorganic anions in sulfonated kerosene.

To sum up, although people have carried out a large number of studies to solve the problem of the purification of inorganic salts in industrial inorganic salts wastewater, and have achieved a lot of research results, these studies have not applied enough materials such as resin, which has the advantages of good operation stability and long service life in sewage treatment. Mixing the resin with some alkali solution to design the purification material may have better application potential, which is the starting point of this research.

3. Alkaline salt solution resin (ASSR) design for ISW treatment

Ion exchange reaction is a reversible reaction, and the exchange ability of ion exchange resin (IER) can be restored by using this reversibility [10–12]. IER has different selectivity for different ions. For mixed ions entering the resin, the resin will have strong adsorption for some ions, but poor adsorption for other ions [13,14]. The size of the ion-exchange affinity is usually related to the ionic radius, hydrated ions, and the number of charged ions [15]. The main regeneration methods are static and dynamic, and dynamic regeneration is generally used to regenerate IER [16]. The selection of regenerant is related to the target ion to be removed, and appropriate regenerant should be selected to achieve the best economic and environmental benefits [17,18]. The regeneration of IER also belongs to the ion exchange process, which conforms to the principle of ion exchange adsorption sequence. The group ions in the IER itself have a greater impact on the regeneration efficiency, and ions with weak adsorption capacity need to use a higher concentration of regenerator. The choice of resin and the use of regenerant need to be balanced to achieve the best benefit. Therefore, to improve the effectiveness and cost performance of ionic solution resin treatment of ISW, a new ASSR material is designed.

3.1. Selection of ASSR materials and conventional regeneration technology

Now, it needs to find a suitable mixed desalting resin which is a material needs to maintain the advantages of ion exchange desalination, but also reduce or eliminate the disadvantages of ion exchange desalination. This resin can provide a new treatment idea for the treatment of wastewater with low salt content and high calcium magnesium and sulfate content. IER can be divided into gel type and large pore type according to pore size. Although large pore type sacrifices part of capacity, it greatly improves ion exchange efficiency due to its increased resin surface area. The specific difference between the two is shown in Fig. 1.

Resin can be divided into cationic resin (CR) and anionic resin (AR) according to the chemical active group, of which CR includes strong acid type and weak acid type, AR includes strong base type and weak base type. The free group dissociation ability of strong acid type CR and strong alkali type AR is very strong, but the regeneration requires high concentration of regeneration liquid. The free group dissociation ability of weak acid type CR and weak alkali type AR is weak, which has certain requirements on the pH of environmental water when working normally. Weak acid CRs do not perform ion exchange at low pH, similarly, weak base ARs do not work at high pH, but they do not require a high concentration of regenerated liquid to regenerate. Specific functional groups are shown:

In ion exchange, when most of the surface free radicals are exchanged, the ions to be exchanged will cross the surface of the resin into the interior, exchange with the internal free groups, and then diffuse back into the solution. This process is relatively slow, and the time consumed is closely related to the structure of the resin. Resins with larger pores and more pores take less time in this process. Therefore, for ion exchange desalination, the selection of highly efficient macroporous resins is a wise choice.

The basic principle of IER desalination is that the cationic ions are exchanged with exchangeable ions with the same charge in the solution, and the different inorganic salts in the water are converted into specific cationic ions carried by the resin. These ions in the water to produce water, gas or solid precipitation reaction, to achieve the purpose of removing salt in the raw water. This means that a pair of cation and IERs need to be selected in the reaction, and the free groups carried by them can react to produce water molecules or other substances that are insoluble in water or can be quickly separated from water, to achieve desalination. Therefore, the combination of hydrogen ions and hydroxide to produce pure water becomes the most direct and observable choice, and the reaction of CR is shown in Eq. (1).

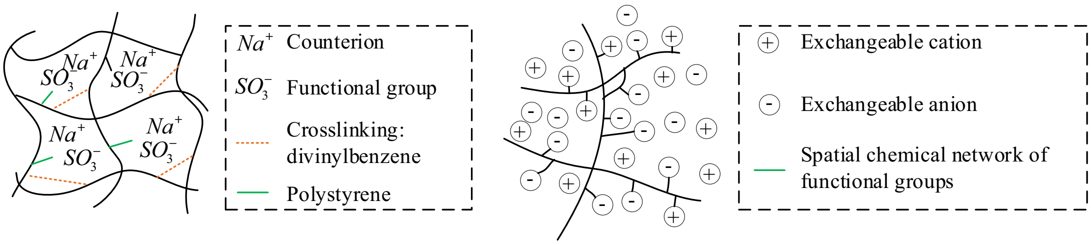
$$n\overline{\mathrm{SO_3H}} + \mathrm{C}^{n+} \rightarrow \overline{\left(\mathrm{SO}_3^-\right)_n \mathrm{C}} + n\mathrm{H}^+ \tag{1}$$

where n means several corresponding objects; $\overline{\mathrm{SO_3H}}$ expresses a sulfonic acid-type strong acid positive resin functional group; C^{n+} denotes a cation with n positive charges; $\overline{\left(\mathrm{SO}_3^-\right)_n \mathrm{C}}$ denotes a polymer composed of sulfite and carbon ions; H^+ represents hydrogen ions. For the reaction equation of AR, Eq. (2).

$$n\overline{\mathrm{ROH}} + \mathrm{A}^{n-} + n\mathrm{H}^+ \rightarrow \overline{\left(\mathrm{R}^+\right)_n \mathrm{A}^{n-}} + n\mathrm{H_2O} \tag{2}$$

where $\overline{\mathrm{ROH}}$ expresses the alkane alcohol polymer; R^+ refers to the general ionic formula of hydrocarbon group or alkyl group; A^{n-} stands for the anion with n negative charge, and $\mathrm{H_2O}$ indicates the chemical equation of water molecule. The disadvantages of this ion exchange desalination method are obvious: regeneration requires high concentration of hydrogen ions and hydroxide solution, resulting in strong acid and alkali waste liquid that is easy to produce drugs, has great environmental impact and is difficult to deal with, and the regeneration liquid is strictly controlled; At the same time, the exchange capacity of the CR is much higher than that of the AR, and the CR is affected by anion more obviously, resulting in a large pH change of water production. The weak acid type CR is weak in dissociation and preferentially adsorbs hydrogen ions to eliminate the temporary hardness in water. The use of weak acid type CR, CR regeneration liquid can be configured with low concentration of strong acid solution, thereby reducing the use of strong acid solution, reduce environmental pollution. Therefore, the predecessors also design a new strong alkali type AR, the free group is bicarbonate ion, and the regeneration solution uses high concentration sodium bicarbonate solution. Compared with traditional high-concentration sodium hydroxide regenerated AR, sodium bicarbonate solution has less environmental impact and is easier to purchase. The desalting reaction of the CR of this new strong alkali type AR is shown in Eq. (3):

$$n\overline{\mathrm{ROOH}} + \mathrm{C}^{n+} \rightarrow \overline{\left(\mathrm{ROO}^-\right)_n \mathrm{C}^{n+}} + n\mathrm{H}^+ \tag{3}$$



(a) Macroporous resin structure

(b) Structure of gel resin

Fig. 1. Structural difference between (a) macroporous resin and (b) gel resin.

where $\overline{\mathrm{ROOH}}$ means the general equation of monocarboxylic acid, and ROO^- expresses the monocarboxylic acid radical. The corresponding AR reaction is denoted in Eq. (4).

$$n\overline{\mathrm{RHCO}_3} + \mathrm{A}^{n-} + n\mathrm{H}^+ \rightarrow \overline{\left(\mathrm{R}^+\right)_n \mathrm{A}^{n-}} + n\mathrm{H}_2\mathrm{O} + \mathrm{CO}_2 \uparrow \qquad (4)$$

where RHCO_3 stands for the general equation of bicarbonate and CO_2 denotes the chemical equation of carbon dioxide. In summary, this study selects strong alkali type AR with bicarbonate radical free group and weak acid type CR with large pores as raw materials for wastewater treatment.

After the resin material is selected, it is necessary to perform experiments to verify the penetration and regeneration properties of the resin. First of all, it is necessary to design the experimental scheme. 15 mL CR and 15 mL AR are respectively loaded into two inorganic glass columns, and a peristaltic pump connected with a rubber hose is adopted. The structure of the experimental equipment is indicated in Fig. 2.

The penetration experiment of low salt wastewater with resin is carried out. The CR and AR are regenerated with different concentrations of hydrochloric acid and sodium bicarbonate. The penetration flow rate is set to 5 mL/min, and the contact is 3 min. The flow rate of the regenerated solution is set to 1.5 mL/min and needs to be touched for 10 min. A simulated wastewater containing 355 mg/L chloride ions, 96 mg/L sulfate ions and 150 mg/L bicarbonate ions is used to carry out the experiment. After regeneration, the penetration experiment is continued and repeated 3 times. Since the main anions of the simulated wastewater are chloride ions, sulfate ions and bicarbonate ions, and the free group of the resin used is bicarbonate ions, the capacity of the AR can be approximated as the sum of the molar quantities of chloride ions and sulfate. The change trend of chloride ion and sulfate ion in the penetration, the total amount of sodium ion and calcium and magnesium in the cationic waste liquid in the regeneration, and the total amount of chloride ion and sulfate ion in the anionic water in the regeneration are determined, to determine the water regeneration efficiency of the resin.

3.2. Design of gas regeneration method for ASSR

The regeneration of ionic solution resin for ISW treatment has an important impact on the continuity and operating cost of wastewater treatment. In the process, due to the selection of large pore weak acid AR adsorption of hydrogen ions is the strongest, even in weak acid water can be regenerated. Therefore, weak acid solution with lower acidity and harm can be selected for CR regeneration. In the weak acid solution, carbonic acid as an inorganic weak acid, compared with other common weak acids, carbonic acid can be spontaneously decomposed into carbon dioxide and water in the outdoor through reversible reaction, which has a low impact on the environment and does not produce gases and liquids with obvious toxicity. However, because of the reversible reaction characteristic of carbonic acid solution, it is difficult to preserve. At the same time, the preparation of carbonic acid solution is relatively simple. Just mixing carbon dioxide gas and water in a confined space can form carbonic acid aqueous solution. The process of preparing carbonic acid aqueous solution can be described by Eq. (5).

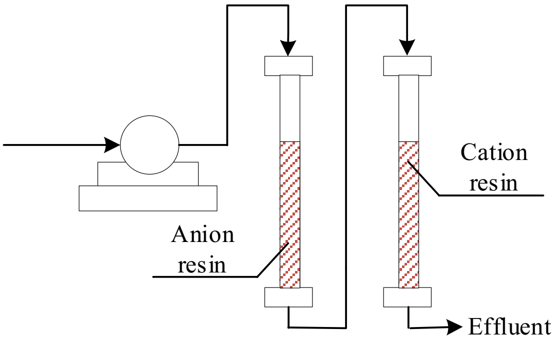


Fig. 2. Schematic diagram of conventional regeneration device for resin materials.

$$\mathrm{CO}_2(\mathrm{g}) + \mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{H}_2\mathrm{CO}_3 \qquad (5)$$

where $\mathrm{H}_2\mathrm{CO}_3$ expresses the chemical equation of carbonic acid. The dissociation of carbonic acid in water also occurs, resulting in the formation of hydrogen ions and bicarbonate ions, as expressed in Eq. (6).

$$\mathrm{H}_2\mathrm{CO}_3 \leftrightarrow \mathrm{H}^+ + \mathrm{HCO}_3^- \qquad (6)$$

First of all, bicarbonate will produce secondary dissociation in water, forming hydrogen ion and carbonate, but the product content of secondary dissociation is very low compared with that of primary dissociation, which is chosen to be ignored here. Compared with other high-concentration weak acid solutions, carbon dioxide gas costs less and is easy to preserve. In resin regeneration, constant carbon dioxide aerosol is applied to a closed regeneration tank filled with neutral water, and through reversible reaction, carbonic acid aqueous solution and carbon dioxide aqueous solution are quickly formed. After passing through CR, the content of hydrogen ions in water is reduced by CR through ion replacement reaction, which tilts the chemical reaction of Eq. (6) to the right and increases the amount of carbonic acid hydrolysis; At the same time, the hydrolyzed carbonic acid content is reduced, tilting the chemical reaction of Eq. (5) to the right, resulting in unused carbon dioxide dissolved in water to participate in regeneration. Because the inlet pressure is constant and the partial pressure of carbon dioxide in the whole reaction chamber is fixed, theoretically the regeneration starts to end, and the overall regeneration rate is maintained at the best speed. By pressurizing, the whole regeneration is more efficient.

In theory, conventional forms of regeneration are not suitable for using carbon dioxide as a regenerator because reversible reaction migration requires waiting for ion diffusion in the solution. However, if the overall regeneration liquid flows through the resin and back into the regeneration tank, the CO_2 utilization can be maximized. In the recycling mode, the contact time between the resin and the regenerated liquid becomes secondary, and the liquid circulation makes the solute distribute evenly. Faster distribution of solutes means an overall increase in regeneration efficiency, maximizing the use of CO_2. In general, the reaction as indicated in Eq. (7) occurs during water production.

$$n\overline{R^+HCO_3^-} + n\overline{RCOOH} + C^{n+}(aq) + A^{n-}(aq) \rightarrow \overline{(ROO^-)_n C^{n+}} + \overline{(R^+)_n A^{n-}} + nH_2O + nCO_2 \uparrow \quad (7)$$

where *A* refers to a variety of anions in water, and *C* denotes a variety of cations in water. The gas dissolution reaction as shown in Eq. (8) will occur inside the regeneration tank.

$$\overline{(ROO^-)_n C^{n+}} + \overline{(R^+)_n A^{n-}} + nH_2O + nCO_2(g) \leftrightarrow n\overline{R^+HCO_3^-} + n\overline{RCOOH} + C^{n+}(aq) + A^{n-}(aq) \quad (8)$$

Due to the selection of cyclic regeneration, the ions washed out of the resin will continue to accumulate in the regeneration solution during the regeneration until the regeneration stops. Continuous regeneration of CR is one of the keys to regeneration, and its regeneration is closely related to pH. A lower pH means a higher concentration of hydrogen ions in water, thereby improving the regeneration efficiency and total amount of CR. Therefore, the pH curve in salt solution caused by the change of partial pressure of carbon dioxide is understood experimentally. Because calcium, magnesium and sodium ions are mainly removed in the wastewater desalination, the bicarbonate ion concentration is the highest in the recycling of AR. Therefore, different concentrations of sodium bicarbonate are selected as the test solution, and the pH in the solution tank is measured by changing the partial pressure provided by the high-pressure carbon dioxide cylinder. The equipment structure is expressed in Fig. 3.

Then to design the gas regeneration test and the equipment used, it first needs to connect the regeneration tank with the resin, forming a closed system. The high-pressure carbon dioxide storage tank is connected into the regeneration tank, providing carbon dioxide and maintaining the partial pressure in the tank. By adjusting the water content in the recycling tank, after sufficient time circulation, the regenerated liquid is taken out and the ions contained in it are measured, and the maximum concentration of bicarbonate in the regenerated liquid, the proportion of the regenerated capacity of the CR and the time of the end of the regeneration process are observed when the CR completely stops regeneration. The device structure of the gas regeneration test is expressed in Fig. 4.

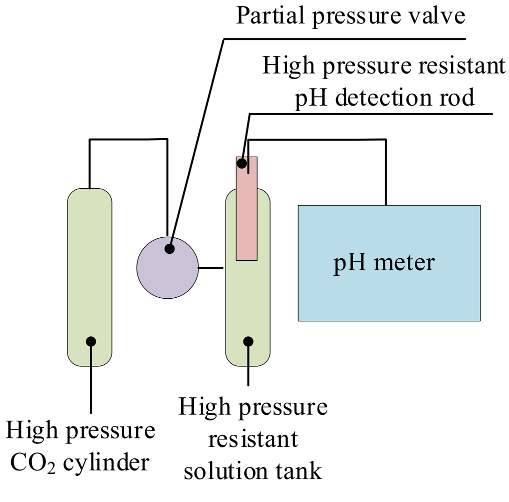


Fig. 3. Test equipment system for pH value of carbon dioxide solution under high pressure.

The device needs to be sealed and stored, and must be able to withstand 1.2 Mpa air pressure, and a plurality of sampling ports are provided on the device to facilitate sampling and measurement at any time. The capacity of the regeneration tank is 1,000 mL, and there are two resin columns that can hold 100 mL resin, which will be used in the subsequent experiment. The experiment uses 0.5% sodium hydroxide aqueous solution as the simulated sewage. The hydroxide ions in the sodium hydroxide solution can neutralize the hydrogen ions produced by the adsorption of the positive resin to form water, and consume the hydrogen ions to quickly penetrate the resin. It washes the resin to neutral with secondary deionized water to avoid the interference of hydroxide ions. In this experiment, the concentration of bicarbonate ion is determined by hydrochloric titration and sodium ion by atomic absorption flame. Bicarbonate can be regarded as the amount of CR regeneration. The penetration flow rate is 33.0 mL/min, and the contact time between water and resin is set to 3 min. The sodium ion content in the water is measured by sampling every 3 min to draw the resin water production curve and observe whether the adsorption capacity of the resin decreases with the increase of the number of carbon dioxide regeneration.

The next step is to design gas series regenerated resin performance verification experiment. The experiment uses 100 mL CR and 100 mL AR, the partial pressure of carbon dioxide is 1.0 Mpa, and the simulated wastewater contains 360 mg/L chloride ions and 98 mg/L sulfate ions. Although recycling can maximize the efficiency of carbon dioxide use, the elution ion accumulation causes the amount of regeneration to not reach the total resin capacity. The data of gas regeneration of CR alone shows that more regenerated liquid has more obvious effect, so the experiment is divided into two schemes: scheme one: Use 500 mL of regenerated liquid to regenerate the fully penetrated cationic exchange column, and take samples every 20 min to detect chloride ions, bicarbonate ions and sulfate ions. When the ion concentration in the tank is basically stable, the regeneration ends. The resin was then penetrated with simulated wastewater, the contact time was maintained for 3 min, and the

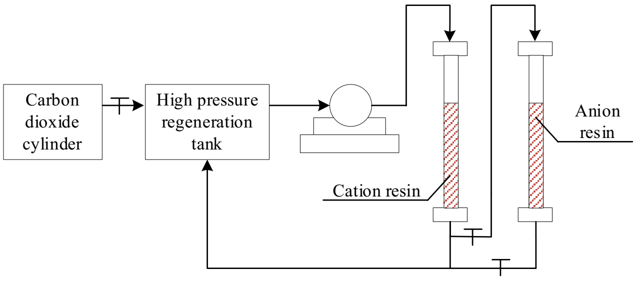
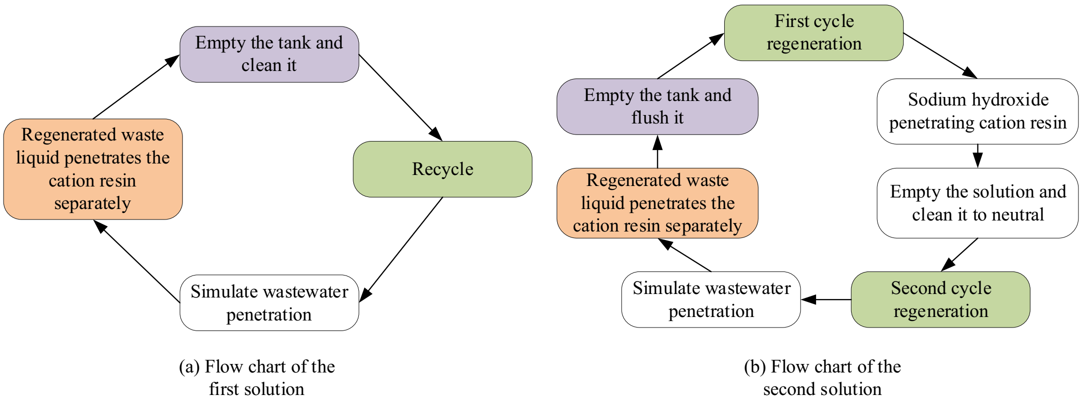


Fig. 4. Device structure diagram of gas regeneration test.

sample was measured every 30 min. After the end of penetration, the waste liquid is used to re-penetrate the positive resin. After the resin was completely penetrated, the test was repeated to verify the universality of the data. Plan 2: After the first round of recycling, drain all the regenerated liquid, use 0.5% concentration of sodium hydroxide solution to penetrate the positive resin, rinse until the pH is neutral. Then a second round of serial regeneration is carried out, and samples are taken every 20 min to measure chloride, bicarbonate and sulfate ions. When the ion concentration in the tank is basically stable, the regeneration is stopped. After that, it penetrates into plan 1, penetrates the CR alone, and finally verifies the repeatability. The flow of the two experimental schemes is shown in Fig. 5.

A regeneration scheme combined with the two schemes in Fig. 5 is designed. In this scheme, a small amount of anion conventional regeneration liquid is introduced into the anion exchange column separately, and the deep regeneration of the anion column is achieved after carbon dioxide regeneration. Conventional regenerated waste liquid is mixed with carbon dioxide recycling waste liquid to be used as anion penetration fluid. Theoretically, the water sample after penetration has a neutral pH, the main ions are calcium, magnesium, sodium, chlorine and sulfate ions, and the environmental impact is small. However, in the conventional regeneration, the regeneration in the resin column is not uniform. The high degree of regeneration is at the bottom, and the low is at the top. The carbon dioxide regeneration cycle will make the regeneration degree of the resin evenly distributed, resulting in the curve of the subsequent conventional regeneration that is inconsistent with the conventional regeneration part of the joint regeneration. Therefore, experiments are designed to observe the actual regeneration situation and achieve the purpose of comparing the regeneration efficiency with that of conventional regeneration methods. The test flow of this scheme is shown in Fig. 6.

The experiment was divided into two conditions: one is conventional regeneration after a single cycle, and the other is conventional regeneration after two cycles. Therefore, it is necessary to set three beds with 2% sodium bicarbonate regenerated solution and two beds with 3% sodium bicarbonate solution to form a comparison group to carry out the experiment. Considering the experimental conditions and purposes, the specific data design: 100 mL CR and 100 mL AR are selected, and the partial pressure of carbon dioxide from the gas is 1.0 Mpa, and the process is the same as the previous experiment. After the resin column is emptied, the AR column is immediately regenerated conventionally. The conventional regeneration method is dynamic, the flow rate is 10 mL/min, and the contact time between the regenerated liquid and the resin is 10 min. It samples the effluent every 5 min to measure the chloride ion and sulfate



(a) Flow chart of the first solution

(b) Flow chart of the second solution

Fig. 5. Experimental process for performance verification of two gas series regeneration resins.

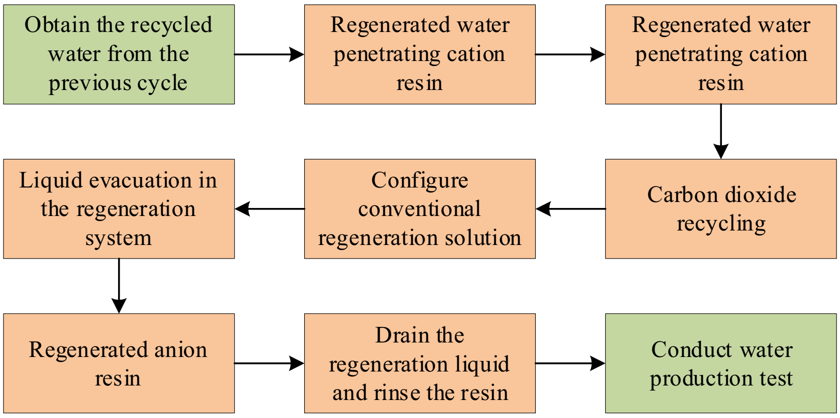


Fig. 6. Experimental process for performance verification of mixed gas series regeneration resin.

content. After regeneration, the water production experiment is carried out with CR, and the simulated wastewater contains 360 mg/L chloride ions.

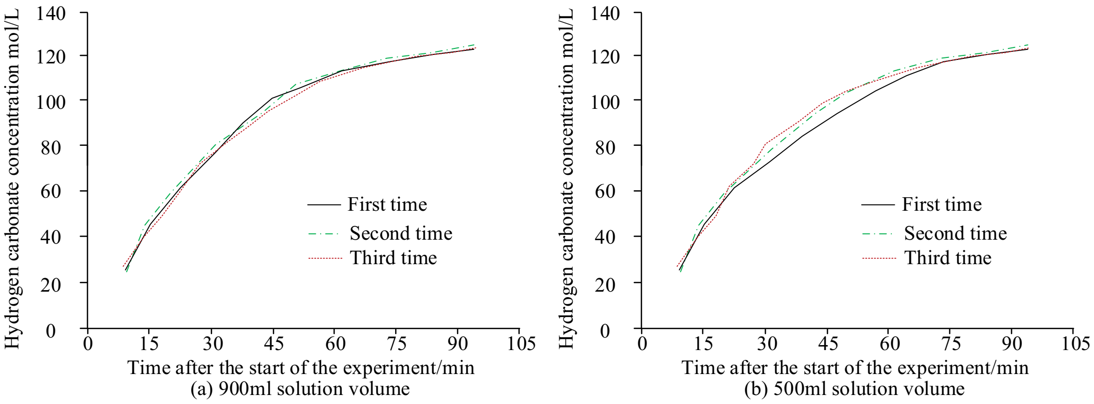
4. Testing experiment of ISW treatment capacity of ASSR

To test the core basic properties of ASSR materials and the ability of ISW treatment, experiments were now carried out in accordance with the established program, and the effluent from an urban sewage treatment plant was selected for field verification experiments. ROMM and MLCO technology were selected as the comparison methods. Comparative wastewater treatment methods were set up in a manner common in the industry.

4.1. Analysis of experimental results of gas regeneration

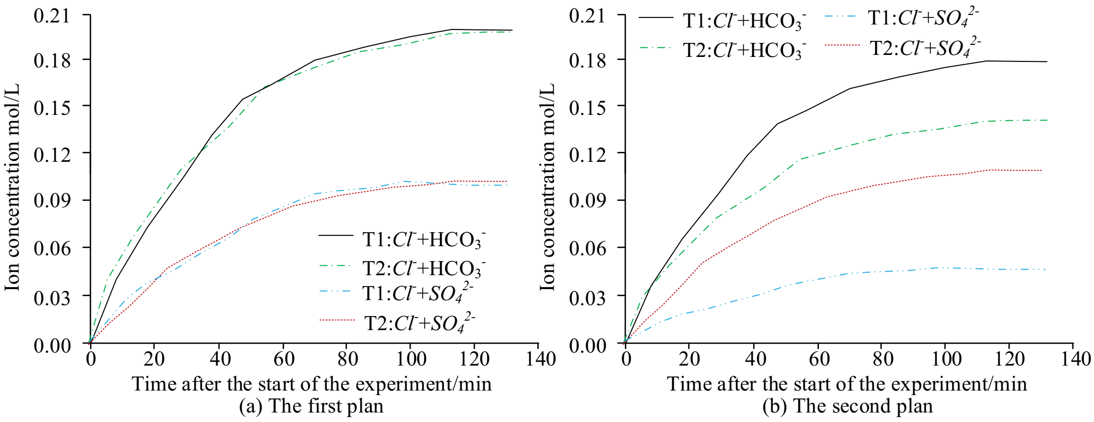
Firstly, the results of the gas regeneration experiment were analyzed. The change curve of ion molar concentration in the tube obtained according to the solution volume of the regeneration tank of 500 and 900 mL is shown in Fig. 7. The horizontal and vertical axes of the two subgraphs in Fig. 7 are consistent, respectively representing the time after the start of the experiment and the molar concentration of bicarbonate in the solution, in min and mol/L, respectively. Different style curves were used to distinguish between different test times. From Fig. 7, under the conditions of 500 and 900 mL solution volume in the regeneration tank, the molar concentration of bicarbonate particles in the solution of each experiment increased gradually with the increase of experiment time, but the molar concentration of bicarbonate particles in the regenerated aqueous solution under each experiment number was slightly different in the end. For example, 100 min after the start of the experiment, the molar concentration of bicarbonate obtained in the first experiment was 122 and 123 mol/L, respectively, when the volume of the regenerated tank solution was 500 and 900 mL. That is to say, within a reasonable range, the volume of the regeneration tank would not have a significant impact on the concentration of bicarbonate in the regeneration liquid. Similarly, the relationship between the sodium ion concentration of the penetrating effluent and the data of the unit bed under the condition of the solution volume of the two regeneration tanks was calculated. The calculation findings denoted that the regeneration of CR could not be achieved by carbon dioxide regeneration, but the regeneration rate was close to 100%. It showed that the recycling rate of carbon dioxide as CR in inorganic salt solution wastewater was very high, and the selection result was reliable.

The change of the total concentration of various main inorganic salts in the two-gas series regeneration resin schemes with the experiment time is shown in Fig. 8.



(a) 900ml solution volume
(b) 500ml solution volume

Fig. 7. Ion variation curves in the tube under (a) 900 mL and (b) 500 mL solution volume conditions.



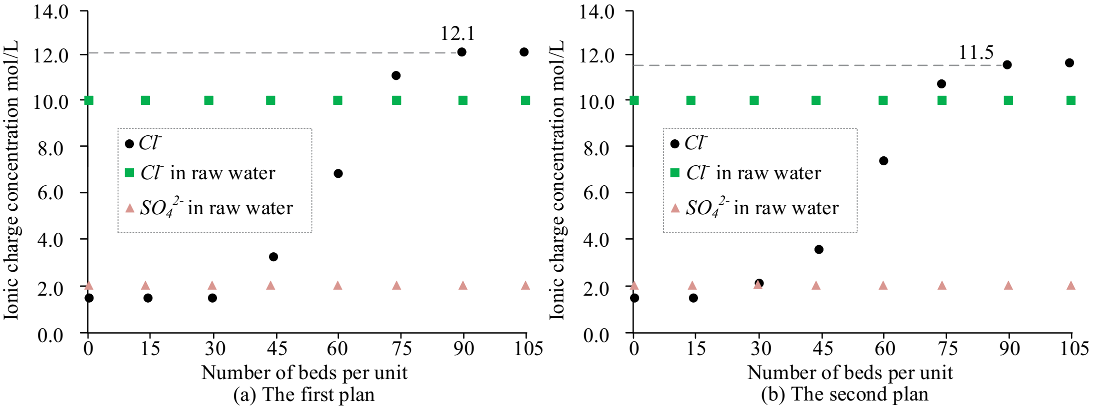
(a) The first plan
(b) The second plan

Fig. 8. Total concentration variation curve of inorganic salt ions in two gas series regeneration resin schemes.

Different subgraphs in Fig. 8 represent different experimental schemes, different linear lines represented different experimental times and ion concentrations. "T_1" and "T_2" expressed the first and second-layer regeneration processes, respectively; "$\text{Cl}^- + \text{SO}_4^{2-}$" and "$\text{Cl}^- + \text{HCO}_3^-$" meant the total concentrations of chloride ions and sulfate ions, and the total concentrations of chloride ions and bicarbonate ions, respectively. From the observation of Fig. 8, in the first scheme, the change law of the corresponding total ion concentration in the solution was slightly different between the first regeneration and the second regeneration. In the second scheme, the change of the total ion concentration in the solution was very different between the first and the second regeneration. In the second scheme, the sum of chloride ion and bicarbonate ion concentration was higher in the first regeneration, and the sum of chloride ion and sulfate ion concentration was higher in the second regeneration, with the highest values of 0.18 and 0.10 mol/L, respectively.

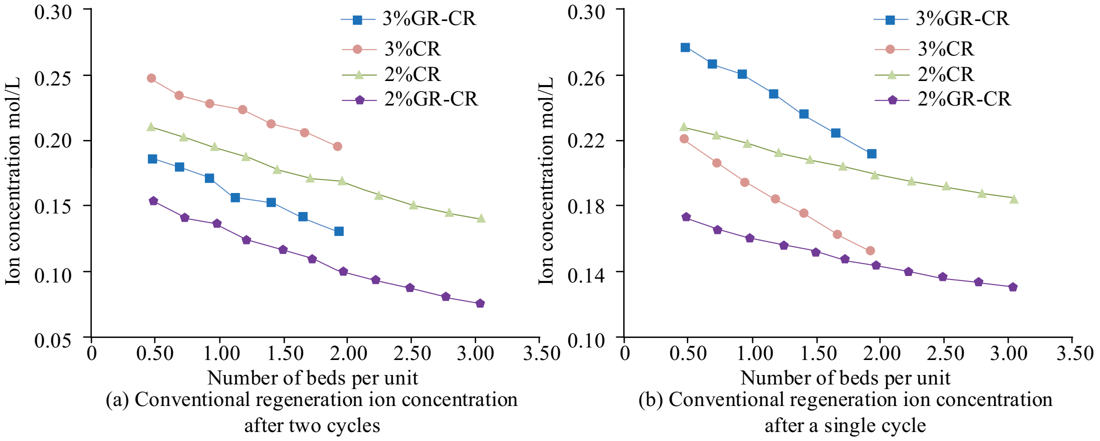
The change of ionic charge concentration in the penetrating water of the two schemes was also counted, as shown in Fig. 9. The vertical axis in Fig. 9 was the same as in Fig. 8, and the horizontal axis represented the amount of beds per unit. From Fig. 9, when the concentrations of chloride ions and sulfate ions in raw water remain unchanged, the change rules of chloride ion concentration in the penetrating effluent of the two schemes were basically the same. With the increase of the amount of beds per unit, the change of chloride ion concentration in the penetrating effluent showed a law of maintaining no movement, then rapidly increasing, and then gradually converging. The maximum chloride ion concentration in the final solutions 1 and 2 was 12.1 and 11.5 mol/L, respectively.

Then, the change of ion concentration of solution in the joint regeneration scheme was calculated, as shown in Fig. 10. Where, "GR-CR" indicated the scheme for conventional regeneration after gas regeneration and "CR" denoted only conventional regeneration. The percentage figure in front of the icon scheme was the concentration of gas in the regeneration process, and different subgraphs referred to different regeneration cycles. From Fig. 10, under the condition of two cycles of regeneration, the ion concentration of the scheme with only 3% concentration was the highest overall. When the unit bed size was 2.00, the ion concentration of the scheme was 0.20 mol/L. Under the condition of single cycle regeneration, the ion concentration of gas regeneration and conventional regeneration only according to 3% concentration was the highest overall, and the ion concentration of this scheme was 0.21 mol/L when the



(a) The first plan (b) The second plan

Fig. 9. Curve of ion charge concentration change in permeate water of two gas series regeneration resin schemes.



(a) Conventional regeneration ion concentration after two cycles (b) Conventional regeneration ion concentration after a single cycle

Fig. 10. Ion concentration variation curve of the combined regeneration scheme: conventional regeneration ion concentration after (a) two cycles and (b) a single cycle.

unit bed was 2.00. After the completion of carbon dioxide regeneration, even if the same regeneration liquid was used and the ratio of the same resin to the conventional regeneration degree was set, the corresponding regeneration effect was worse than that of the scheme data using the conventional regeneration method alone.

4.2. Analysis of ISW treatment results based on examples

The wastewater discharged from the sewage treatment plant as an example contained inorganic salts composed of more chloride ions, which met the application conditions of the treatment method designed in this study. In the initial experimental design, the water production flow rate of the object was 8 m^3/h. 2.7 m^3 sodium hydroxide solution with 2% concentration and 2.0 m^3 2% concentration of CR were added to the recycled negative resin. The designed water production rate was about 90%, and the treatment goal was to reduce the chloride ion concentration to 250 mg/L. The water produced from the sewage treatment plant would be evenly introduced into the treatment process equipment designed in this study and the other two comparison method equipment for comparative purification experiment. The comparison results of equivalent chloride ion concentration in effluent of this research design process under different regeneration water consumption are shown in Table 2. From Table 2, for the first regeneration condition, the regeneration amount of resin was 0.75 mol/L, but in the second regeneration, the regeneration amount dropped to 0.72 mol/L, and in the third regeneration, this data was 0.69 mol/L. This indicated that the capacity of resin would decrease in the first two regenerated processes. Considering the overall number of regeneration, it was most reasonable to set three times, because the cost of comprehensive wastewater treatment was lower and the degree of material utilization was higher.

According to the statistics of the conditions of three regenerations, the effluent pH under various treatment processes is shown in Table 3. The "Improving Salt Solution Resin" (ISSR) in Table 3 indicated the process designed in this study. From the observation of Table 3, the effluent pH of the ISSR process at the beginning was low, 5.5, because there was still part of hydrochloric acid regeneration liquid in the CR at the beginning. With the growth of

Table 3
pH of effluent under various treatment processes

Experiment number	Time after the start of the experiment/min	ISSR	ROMM	MLCO
001	20	5.5	6.2	6.6
002	50	6.6	6.5	6.8
003	80	6.7	6.5	6.8
004	110	6.8	6.7	6.4
005	140	7.0	6.6	6.2
006	170	6.8	6.2	6.0
007	200	6.5	6.0	5.9
008	230	6.2	5.9	5.9
009	260	6.1	5.8	5.8
010	290	6.0	5.8	5.7

Table 1
Types of IERs and adsorption priority order

Classification number	Name	Adsorption sequence	Functional groups
#01	Strong acid cation resin	$Fe^{3+} > Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+ > H^+$	Sulfonic acid group
#02	Weakly acidic cation resin	$H^+ > Fe^{3+} > Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+$	Phosphoric acid group, carboxylic acid group, etc.
#03	Strong alkaline anion resin	$SO_4^{2-} > NO_3^- > Cl_3^- > OH^- > F^- > HCO_3^- > HSiO_3^-$	Quaternary amino group
#04	Weakly alkaline anion resin	$OH^- > SO_4^{2-} > NO_3^- > Cl_3^- > HCO_3^- > HSiO_3^-$	Primary amino, secondary amino, tertiary amino, etc.

Table 2
Equivalent chloride concentration under different regeneration conditions (in mg/L)

Experiment number	Regenerative water consumption/m^3	First regeneration	Second regeneration	Third regeneration
01	0.4	1,085	1,082	1,069
02	0.8	7,385	6,941	6,235
03	1.2	5,890	5,613	5,244
04	1.6	4,671	4,608	4,662
05	2.0	4,360	4,363	4,122
06	2.4	3,516	3,519	3,485
07	2.8	2,983	2,904	2,976
08	3.2	2,324	2,306	2,315

the experiment, the effluent pH began to rise and stabilized around 6.8, and then gradually decreased. The pH range of residential water was 6.5~8.5. From Table 3, the pH of the effluent from ISSR, ROMM and multi-stage contact oxidation (MLCO) process was in this range for a maximum of 150, 120 and 110 min, respectively.

Then, according to the established wastewater purification target as the indicator of whether the wastewater was qualified for purification, the effluent was sampled every 10 min, and the sampling was repeated 10 times in each round of experiments. To further improve the statistical accuracy, each experimental scheme was repeated 5 times, and the results were presented according to the mean value and standard deviation. The ion concentration values of various process effluent under different raw water ion concentrations were calculated, as shown in Fig. 11. Where, "ROMM" and "MLCO", respectively represent reverse osmosis membrane method and multi-stage contact oxidation, and different ICONS represent different processing processes. The gray virtual line is the auxiliary line. It can be seen from Fig. 11 that, on the whole, the effluent qualification rate of each process decreases with the increase of raw water ion concentration. However, for ISSR method and ROMM method, when the primary ion concentration is less than 0.10 and 0.06 mol/L, the corresponding qualification rate of effluent is 100% without standard deviation. When the ion concentration is greater than 0.04 mol/L, the qualified rate of the effluent by ISSR method is higher than that of all comparison processes.

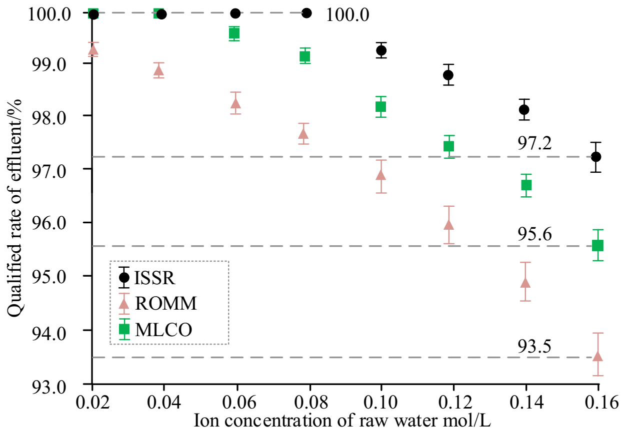


Fig. 11. Ion concentrations of various process effluents under different raw water ion concentrations.

Finally, the variation of chloride ion concentration in each process after repeated water production and stabilization was calculated, as shown in Fig. 12. Where, the chloride ion concentration in raw water was maintained at about 360 mg/L. When the number of beds per unit was less than 80, the ion concentration of the effluent rate of each process changed slightly, and was less than the effluent qualified standard 250 mg/L. Specifically, when the unit bed was less than 80, the average chloride ion concentration of ISSR, ROMM and MLCO effluent was 47, 92 and 78 mg/L, respectively. Then, with the increase of unit bed, the chloride ion concentration in the effluent of each process began to rise rapidly.

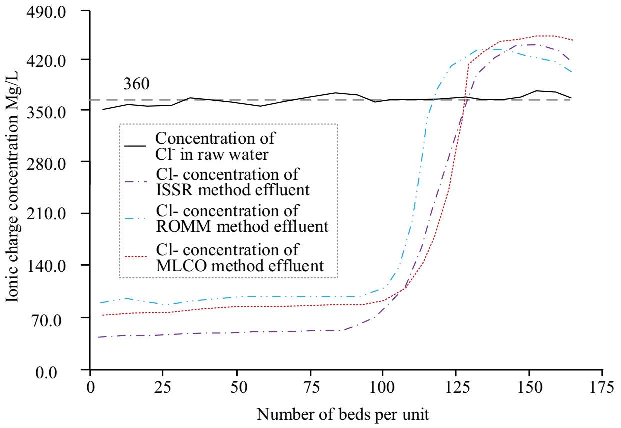


Fig. 12. Comparison of ion concentration changes in various processes after stable water production.

5. Conclusion

In this study, a kind of ASSR material, which was mixed with sodium bicarbonate, strong alkali type AR with free group of bicarbonate root and weak acid type CR with large pore, was designed for the treatment of ISW. To debug a better material ratio, gas regeneration experiments were carried out, and to test the wastewater treatment capacity of this material, a sewage treatment plant was selected to carry out wastewater purification experiments. The research findings denoted that under the conditions of 500 and 900 mL solution volume of the regenerated tank, the molar concentration of bicarbonate particles in the solution increased gradually with the increase of experiment time, but the molar concentration of bicarbonate particles in the solution under each experiment number was slightly different. In other words, within a reasonable range, the volume of the regeneration tank would not have a significant effect on the concentration of bicarbonate in the regeneration liquid. After the completion of carbon dioxide regeneration, the regeneration effect of the combined gas regeneration scheme was worse than that of the scheme using only the conventional regeneration method, even if the same regeneration liquid was used and the ratio of the resin to the conventional regeneration degree was set. The example experiment outcomes indicated that the maximum time for the ISSR, ROMM and MLCO process to have effluent pH in the range of 6.5‘8.5 was 150, 120 and 110 min, respectively, and when the ion concentration was greater than 0.04 mol/L, the effluent passing rate of ISSR method was higher than that of all comparison processes. When the unit bed was less than 80, the mean chloride ion concentration of ISSR, ROMM and MLCO effluent was 47, 92 and 78 mg/L, respectively. The chloride ion inorganic salt removal ability of wastewater of ASSR designed in this study was stronger than that of traditional methods, and the water purification ability lasted longer. However, a shortcoming of this study is that it is not able to test the evolutionary effects of this solution on a wider range of different inorganic salt ions, which will be supplemented in subsequent studies.

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