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ANALYSIS OF EXISTING METHODS FOR IMPROVING THE PHYSICAL AND CHEMICAL CONDITIONS OF THE ION EXCHANGE PROCESS IN WATER TREATMENT

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Abstract

The article deals with the issues of existing processes for improving the physical and chemical conditions of the ion exchange process in water treatment. Patents and publications on the use of the ion exchange method in water treatment have been analysed. The expediency and scientific significance are determined by the possibility of further improving the efficiency of the ion exchange process in water treatment on the basis of the obtained results.

Existing methods, such as thermal and cryogenic treatment, membrane plants, distillation and reverse osmosis, have a number of disadvantages, such as high energy consumption of the process and the inability to be used on an industrial scale. A promising method to improve the efficiency of modified ion exchange resins is to use the effect of a magnetic field on the feed water with constant stirring.

The article analyses ion exchange resins and their problems, existing research aimed at modernising the ion exchange process, considers ways to optimise the selectivity of ion exchange resins, their modification with dendritic aggregates, and the use of mixed cationic and anionic ion exchange resins. Regeneration of ion-exchange resins using ammonium bicarbonate technology, reagent-free regeneration methods, such as electrodialysis, electroionization systems, in order to reduce process waste, possible schemes of using ion-exchange plants in combination with other methods of water treatment.

The analysis shows the relevance of using the ion exchange process in water treatment and the prospect of further research on ways to intensify the process to reduce energy and economic resources.

The obtained results demonstrate the most advanced ways to improve the method of ion exchange for water treatment, such as reagentless regeneration of ionites using electrodialysis, modification of resins by introducing the necessary functional groups.

Key words: ion-exchange resins, electrodialysis, regeneration, water treatment, cationite, anionite, sorption, selectivity.

1 Problem statement

Water is a vital resource that sustains life, and ensuring its quality is crucial for public health and environmental protection. One of the most common methods of water purification is ion exchange, a process that relies on the ability of ion exchange materials to absorb positive or negative ions from water in exchange for an equivalent amount of heavy metal ions. The main problems of the ion exchange process are: the constant cost of renewing all chemical reagents and the need to dispose of used reagents.

Modern methods of improving the process of ion exchange in water treatment are aimed at reducing energy consumption and costs for the restoration of system components, upgrading existing ion exchange devices, new schemes for water supply and drainage, the use of regeneration solution, loosening and washing systems for ion exchange material [1].

One example of such methods is the use of the ion exchange method in a complex, which involves the following sequence: mechanical treatment, passing water through a mixed-action ion exchange filter, oxidative treatment with ozone, filtration through activated carbon and filtration through a woven filter. The process of treating water by passing it through a mixed-action ion exchange filter before ozonation has its advantages and disadvantages [2].

The advantage of this method is that cationisation and anionisation take place simultaneously in one filter

layer, which allows the sorption of organic compounds in the form of high- and low-molecular-weight organic acids on anionite and hardness salts on cationite. Also, during the passage through the cationite and anionite layers, the reaction can be controlled, with the possibility of adjusting the pH balance within 6...7 units, which further allows for oxygen treatment under optimal conditions. Changing the pH can make the sorbent more or less selective to certain ions. The disadvantage is that ion exchange resins lose their sorption efficiency due to the content of organic compounds, which can also be retained on their surface when water is passed through at this stage.

Another method is the use of new generation ion exchange resins with weakly dissociated functional groups that have increased sorption capacity and the ability to regenerate almost stoichiometric amounts of acid or alkali [3].

2 Analysis of research and publications

2.1 Ion exchange resins and their problems

Ion exchange resins are cross-linked structures with a strong condensation gel structure, which include silica gel and clay minerals. Depending on the degree of cross-linking, i.e. their number, the average mesh size of the ionite is related [4]. Due to the heterogeneity of the mesh, there are problems with the sorption of sufficiently large, especially high-molecular-weight organic ions, because they get entangled in smaller

cells, thereby blocking the larger ones, preventing the sorption of other, even smaller ions or molecules.

The main characteristics of ion exchange resins include: ion exchange capacity, pore size, nature of counterions, ion charge, polarisation and swelling [5].

Today, the synthesis of resins with crosslinking from long-chain agents is widespread.

The electron microscopic images of such resins are quite similar to those of active carbon. The gel phase (i.e., the solid skeleton of such resins) is highly compressed, because a lot of crosslinking is introduced during the synthesis (18...36 % divinylbenzene). Therefore, even in the swollen state, the cells of the gel phase are quite small. Such resins have obvious pores with a diameter of 200...2000 angstroms, but the size of most of the pores is 150...250 angstroms. The disadvantage of such resins is a noticeable decrease in their volumetric exchange capacity. The system of internal pores and increased specific surface area gives the following advantages:

- ion-exchange ability of resins is manifested in weakly polar solutions, where it was not previously manifested;

- the ability of resins to acid-base catalysis, including in weakly polar solutions, is sharply enhanced;

- the ability of resins to adsorb sufficiently large organic ions and molecules is significantly increased;

- increased mechanical stability of the grain, as well as their resistance to "osmotic shock" is noted;

- sharp repeated changes in the concentration of the external solution.

For conventional resins, this leads to grain cracking due to sudden changes in shrinkage and swelling [3].

Taking into account water treatment systems in which ion exchange is used before biological treatment, synthetic ion exchange resins are used to carry out the ozonation stage under normal conditions [6].

They are typical gels, with a backbone matrix consisting of an irregular, highly polymeric spatial network of hydrocarbon chains. The matrix contains charge-carrying groups, the so-called fixed ions. The properties of synthetic ionomers are mainly determined by the number and type of fixed ions, as well as the structure of the matrix, especially the number of crosslinks in it. The sorption properties of ion exchange resins can be set during the manufacturing process. Ionogenic groups are either introduced into the starting substance before the resin formation process begins or attached to the resin macromolecules. Common resins are phenol-formaldehyde, polystyrene cationic, amino-formaldehyde, polyamine and polystyrene anionic.

An ionite can adsorb a certain number of ions from an electrolyte solution that have the same charge of the same sign as the charge of the functional group ion. These sorbed ions are called cations. They can form chemical compounds with the ions of opposite charge that have been absorbed, i.e., a part of the electrolyte is sorbed from the solution. If the number of cations is small, they can be neglected as they will not have a significant effect.

Equally important when analysing the problems of the ion exchange process is the need to take into account

the factors that affect the exchange capacity of ionites. The degree of utilisation of the exchange capacity of an ionite depends on the size and shape of the grain. Typically, the grain size is in the range of 0.5...1 mm. The shape of the grain depends on the method of preparation of the ionite. They can be spherical or oval. The spherical shape is preferred because they have an even shape and the same size, which ensures uniform exchange of water ions [7].

Ionites with cylindrical grains, fibrous ionites and others are also used. The finer the grains, the better the exchange capacity of the ionite is used, but depending on the equipment used, either the hydraulic resistance of the sorbent layer increases or small ionite grains are carried away by the solution. Therefore, in the synthesis of ion exchange resins, the required grain size is determined depending on the task at hand, in conjunction with the choice of ionite loading method and system.

2.2 Particle size of ion exchange resins

The use of ion exchange resins with a specific particle size can affect the rate and efficiency of ion exchange. Smaller particles can provide a larger binding surface, but they can lead to a loss of pressure in the system.

One way to prevent the removal of ion exchange material is to use ion exchange resins that contain ferromagnetic impurities. This allows to retain the fine-grained material in a suspended state in the zone of the magnetic field through which the solution moves [3].

2.3 Ways to improve the ion exchange process.

Improving the selectivity of sorbents during the ion exchange process is important for effective water treatment, as it helps to remove specific ions from the solution without undue impact on other components. Here are some examples of technologies and methods that help to increase the selectivity of sorbents:

Selectivity is based on the nature of the material.

Some sorbents have properties that make them selective to certain ions. For example, ions with amine groups can be selective for certain metals [7].

Modification of the sorbent. Changing functional groups – replacing or adding functional groups to the surface of a sorbent can increase its selectivity. For example, modifying a sorbent with sulpho groups can make it selective for metal cations.

Optimising the pH of the medium. Adjusting the pH of the water can affect the charge of ions and their ability to bind to the sorbent. To improve ion exchange, it can be important to maintain the optimum pH value for a particular sorbent and ion type.

The use of solvents, inert salts and buffer solutions are important methods for optimising the pH of the medium during the ion exchange process in water treatment. They allow controlling and maintaining the required pH value of the medium for the effective implementation of ion exchange [8].

Acids (e.g., hydrochloric acid – HCl) and alkalis (e.g., sodium hydroxide – NaOH) can be used as pH adjusting agents. Adding an acid lowers the pH, while adding an alkali raises it. This is useful for correcting the pH when it is necessary to change the environment in the system.

Inert salts, such as NaCl, have no effect on pH. This salt can be used to increase the ionic strength of a solution, which is useful during ion exchange. Another inert salt is potassium chloride (KCl), which can be used to increase the ionic strength without affecting the pH.

Buffer solutions have the ability to maintain a stable pH value. The most commonly used buffers for laboratory analysis are phosphate buffers, acetate buffers and TRIS buffers. The use of buffers avoids sudden changes in pH during the process and provides stable conditions for ion sorption.

Buffers are the most stable in terms of maintaining a stable pH, but they can be costly and require additional treatments.

Acids and alkalis change the pH quickly, so their use can be useful when you need to quickly adjust the environment.

Use of complexing agents. The addition of special reagents that form complexes with the desired ions can change their chemical activity and make the sorbent more selective to other ions.

The formation of reagents to form competitive complexes can be useful in increasing the selectivity of sorbents in ion exchange. These complexes compete with the ions you want to remove or retain and affect their distribution on the sorbent.

Ethylenediaminetetraacetic acid (EDTA) is a powerful complexing agent for many metals. It can be used to form complexes with the metals you want to remove, competing with them for activity on the sorbent. For example, when treating water for heavy metals such as lead or manganese, EDTA can be used to create competitive complexes.

2.4 The process of regenerating ion exchange resins

After the sorbent is saturated with ions and ceases to effectively purify water, i.e. is depleted, a regeneration process is envisaged to restore it.

The process of regeneration of ion-exchange materials is the stage of the sorption-regeneration cycle, which consists of sequential operations leading to the restoration of the original capacity and shape of ionites [9].

The regeneration of ion exchange resins is based on the chemical reaction of the exchange of ions that are displaced and ions that are chemically bound to the functional groups of the resin. The main operations of the regeneration process:

- washing of the ionite after the completion of the sorption cycle;
- loosening of the ionite layer;
- direct regeneration of the ionite;
- washing of the ionite.

The most commonly used regeneration scheme in ion exchange processes is the direct-flow regeneration scheme, which is based on the organisation of the direction of solution flow in the sorption-regeneration cycle. In this case, the direction of flow of the regenerant and the flow from which the component is extracted at the sorption stage coincides.

Counter current regeneration is based on the fact that the regenerate is fed in the direction opposite to the solution to be purified in the sorption stage. Given that

the final part of the ionite layer is regenerated more efficiently during the sorption stage than in the case of direct-flow regeneration, the degree of regeneration of the remaining part of the layer can be reduced due to the consumption of regenerant, however, this regeneration scheme excludes a special operation to stir the ionite layer and increase the hydraulic resistance [10].

Periodic regeneration can be carried out both in dynamic conditions and in a stepwise manner.

Step regeneration and washing means that the filter is alternated between a rapid filling of the filter with a regenerating solution, or water during washing, and the ionite is kept in a stationary liquid for a certain time.

One of the most relevant ways to reduce losses during the regeneration process is recirculation, which involves removing the bulk of the desorbed component at the beginning of the regeneration process. The resulting regenerate is highly concentrated and may contain valuable impurities, which are removed. The remaining portions of the regenerate that pass through the ioniser can be used at the initial stage of the next cycle. This reduces reagent consumption and wastewater generation [3].

Reagent-free regeneration methods are currently being developed. These methods include electrochemical and thermochemical regeneration.

However, electrochemical regeneration is currently used only in ion exchange desalination processes for low-mineralised water, due to the low intensity of the process due to the kinetics controlled by ion diffusion.

Reagentless regeneration is based on a process without the use of chemical solutions and is possible in the case of physical sorption as well as in the case of specific exchange processes. Reagentless regeneration is driven by chemical processes, but unlike reactive regeneration, the regenerating ions are not introduced into the system from the outside but are formed within it (e.g., as a result of the hydrolysis of functional groups).

Among the reagent-free methods of ion exchange resin regeneration, the syrothermal process is a widely used one for desalination of water with a salt content of no more than 3000 mg/dm³ using a specially selected scheme of low-base and weakly acidic ion exchange resins. The sorption process is followed by a regeneration process. The peculiarity of this process is that hot water is used to regenerate the resin saturated with salts. The theoretical capacity of the syrothermal process is about 2 mg-eq/l, but in practice, the capacities achieved to date are much lower and about an order of magnitude less than those of conventional ionisers. The main reasons for the low capacity are the formation of internal salt, low kinetic properties and the type of sorption isotherm.

Thermohydrolytic cleavage of salt forms of a number of ionites can be used for their regeneration. However, the hydrolysis process is reversible and its degree for different salt forms depends on the strength of attraction of counterions to functional groups, which increase with increasing volume of contacting water and temperature, and with decreasing ionisation constants of ionogenic groups of H⁺ and OH⁻ forms of ionites, as well as bases and acids formed during hydrolysis. When the process is carried out under dynamic conditions with

high water and heat consumption, it can lead to an almost complete conversion of the salt form into the acid or basic form, but high costs should be taken into account [11].

The water consumption for regeneration can be reduced by running the process under static conditions and by creating a vacuum. The reduction in equilibrium is not only due to temperature, but also to the removal of volatile compounds. However, this principle is only applicable to salt forms of ionising gaseous products. Increasing the temperature can increase the rate of ion exchange reactions. However, it can also lead to a decrease in sorbent stability, so it is important to find a balance between temperature and stability.

Electrodeionisation is the demineralisation of water streams in an electrically controlled membrane process. Instead of chemicals, electricity is used to regenerate the resin, and ionic and ionising compounds are removed in a continuous process, ensuring a consistently high-quality water treatment process [12].

The advantages of electrodeposition systems include the absence of reagents, automatic regeneration by electric current, reduced waste, the electric field reduces the growth of bacteria in the resin during service, no risk of cross-contamination with other resins, and continuity of operation [13].

Xavier C. and Jhonny V.F. [14] studied the use of bipolar electro dialysis for the production of hydrochloric acid as a result of the regeneration of ion-exchange resins from wastewater.

Electrodialysis is the process of separating ionic substances dissolved in an aqueous solution by applying an electric current in a direction perpendicular to selective ionic membranes that provide selective transport of ions according to their cationic or anionic exchange.

Bipolar membranes are used in combination with ion exchange membranes, alternately placed between two electrodes. They are formed by an anion-exchange membrane and a cation-exchange membrane, which are in direct contact or separated by a porous medium [15]. The intermediate region is called the transition region. These membranes allow the dissociation of water molecules by applying an electric field, generating protons and hydroxyls on the cationic and anionic side, respectively, with less energy consumption than necessary, which has great advantages over chemical regeneration methods.

The requirements for electro dialysis with bipolar membranes, such as the distance between the membranes, the need to install auxiliary separators and the ratio of membrane area to the volume of the system module, are investigated.

The use of bipolar electro dialysis allows for the extraction of chlorine and sodium ions, resulting in the extraction of 84.91 % of chlorine ions for the production of hydrochloric acid, which can be used in the regeneration of strong cation exchange resins, and 39.02 % of sodium ions for the production of sodium hydroxide [8].

Electrodeionisation is known to be used to remove boron and lithium [16] from aqueous solutions. The use of ion-exchange resins in the electrodeposition process reduces the time for ion recovery by reducing the

system resistance. The process reduces electricity consumption and produces hydrogen gas.

The work of Chen X. et al. [17] was considered, in which a new combined layer was proposed for the implementation of highly efficient regeneration of ion exchange resins, in which cationite and anionite are located next to the cationic and anionic membrane and are placed in layers.

The proposed electrodeposition device allows achieving high efficiency of ion exchange resin regeneration along with anti-scaling characteristics. This combined layer can enhance the water dissociation reaction and reduce the number of ion collisions, which makes it possible to replace the traditional chemical regeneration method. The higher amount of anion exchange resin results in an acidic environment, which effectively prevented the formation of scale.

The device can overcome the limitations associated with the conditions of the input water and increase the efficiency of ion exchange resin regeneration, which is favourable for industrial applications of the technology.

2.5 Modification of ion exchange resins.

A promising innovation described in the work of Gettongsong T. et al. [18] is the use of mixed cationic and anionic ion exchange resins. Their advantages in demineralisation of seawater are low inlet pressure, simple setup, and high efficiency.

However, such resins have a limited ability to remove and adsorb ions in seawater or in sufficiently concentrated salt water, as the resource is exhausted when most of the ion-acceptors on the surface of the granules are depleted and no longer adsorb ions in aqueous solution. This problem was proposed to be solved by supporting the separation of the resin into anionites and cationites with subsequent regeneration of each of them with large volumes of strong acid and strong base.

The published results indicate that ammonium bicarbonate can regenerate waste resin without the need to separate cationic and anionic resins, and without the use of strong acid and strong base regeneration. Ammonium bicarbonate, or thermolytic salt, is able to decompose in aqueous solution at low temperatures from 35°C to 80°C [18].

To desalinate water with high salt content, an ion exchange resin was used, which consisted of a chemically crosslinked ampholytic polymer resin or a crosslinked ionic polymer resin that has 2 oppositely charged groups on the same polymer chain, both containing strong acid and base groups on the same polymer chain, which also helps to maintain the pH in the system [19].

The prospect of using magnetic ion exchange resins lies in their differences from traditional resins, namely, smaller granule size, magnetic properties and ease of regeneration with NaCl solution. The adsorption efficiency is influenced by pH, temperature, and ionic composition of water. Removal efficiency [20].

In [21], magnetically modified forms of 13X zeolite were obtained. The properties, ion exchange and magnetic properties of the obtained samples were investigated. The experimental results indicate that the

cation exchange capacity of magnetically modified ion exchange resins is 27 % higher than the cation exchange capacity of unmodified zeolite.

To correct the mineral composition of water, it is advisable to use a modification of ion exchange resins [22, 23], which will reduce the consumption of ion exchange resins by an average of 20...25%, increase the productivity of ion exchange facilities by 19...22 %, and reduce the cost of demineralisation by 15...20 %.

Conclusions

1. The ion exchange process is an essential component of modern water treatment, providing an effective method of removing contaminants and improving water quality. As the demand for clean water continues to grow, the need to improve the physico-chemical properties of ion exchange resins is becoming increasingly apparent.

2. Today, there are ways to physically and chemically improve the ion exchange process in water treatment.

3. The most promising methods identified in the analysis of scientific papers are as follows:

- use of a multi-stage process;
- the use of the ion-exchange method in complex water treatment, or sequential treatment with filters designed to remove different types of ions, leads to better water treatment and reduced consumption of sorbent material;

- the use of bipolar electro dialysis, which allows for the extraction of chlorine and sodium ions, for the subsequent production of hydrochloric acid, which can be used in the regeneration of strong cation exchange resins, reducing the generation of waste from the water treatment process.

- the use of modified resins allows for low inlet pressure, simplified setup, and reduced need for lengthy pretreatment. The prospect of using it as the main method of treating brackish groundwater in remote settlements to replace existing methods that require significant maintenance costs and are more difficult to implement.

4. The most promising in further research will be the use of magnetic activation of ion-exchange resins to adjust the mineral composition of natural waters.

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АНАЛІЗ ІСНУЮЧИХ МЕТОДІВ ПОКРАЩЕННЯ ФІЗИКО-ХІМІЧНИХ УМОВ ПРОЦЕСУ ІОННОГО ОБМІНУ ПРИ ВОДОПІДГОТОВЦІ

У статті розглядаються питання існуючих процесів покращення фізико-хімічних умов процесу іонного обміну при водопідготовці. Проаналізовано патенти та публікації досліджень використання методу іонного обміну при водопідготовці. Доцільність і наукове значення визначається можливістю в подальшому на основі отриманих результатів, підвищення ефективності процесу іонного обміну при водопідготовці.

Існуючі методи, такі як термічна та кріогенна обробка, мембранні установки, дистиляція та зворотний осмос, мають ряд недоліків, у вигляді великої енергоємності проведення процесу, неможливість застосування у промислових масштабах. Перспективним методом підвищення ефективності модифікованих іонообмінних смол є використання дії магнітного поля на вихідну воду при постійному перемішуванні.

У статті проведено аналіз іонообмінних смол та їх проблеми, існуючі дослідження, які направлені на модернізацію проведення іонообмінного процесу, розглянуто способи оптимізації селективності іонообмінних смол, їх модифікація дендритними агрегатами, використання змішаних катіоніт та аніоніт іонообмінних смол. Регенерація іонообмінних смол за допомогою технології бікарбонату амонію, безреагентних методів регенерації, таких як електродіаліз, системи електродеіонізації, з метою зменшення відходів процесу, можливі схеми застосування іонообмінних установок в комплексі з іншими методами очищення води.

Проведений аналіз свідчить про актуальність використання процесу іонного обміну при водопідготовці та перспективу подальших досліджень способів інтенсифікації процесу для зниження витрати енергетичних та економічних ресурсів.

Отримані результати демонструють найбільш розвинені шляхи покращення методу іонного обміну для очистки води, такі як безреагентна регенерація іонітів з використання електродіалізу, модифікація смол введенням необхідних функціональних груп.

Ключові слова: іонообмінні смоли, електродіаліз, регенерація, очистка води, катіоніт, аніоніт, сорбція, селективність.

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