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Promising method of ion exchange separation of anions before reverse osmosis

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Abstract: A method to improve the quality of purified water, reduce the cost of reagents for the regeneration of resin and create low-waste processes have been developed. This paper presents the results of ion exchange separation of sulfates and nitrates using AV-17-8 anion exchange resin in NO_3 form. The efficiency of anion separation on the highly basic anion exchange resin AV-17-8 depends on the magnitude and ratio of their concentrations in water. Separation on the AV-17-8 anion exchange resin has been shown to be effective at concentrations of sulfates up to 800 mg/dm^3 and nitrates up to 100 mg/dm^3 . Conditions for regeneration of 10% NaNO_3 anion exchange resin were determined. Reagent precipitation of sulfates from the used regeneration solution in the form of calcium sulfate was carried out. Calcium sulfate precipitate can be used in the manufacturing of building materials. The regeneration solution is suitable for reuse. The developed results will allow to introduce low-waste desalination technology of highly mineralized waters.

Introduction

Scientific and technological progress, as well as the growth of economic activity cause increasing anthropogenic pressure on the environment nowadays. This leads to the imbalance in the environment and exacerbates socio-economic problems (Berger E. et al. 2019). Therefore, the problems of salinization of natural waters, which are the source of water supply, are becoming more acute (Kaushal S.S. 2016, Dugan H.A. et al. 2017). Common ions associated with anthropogenic salinity include Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- (Griffith M.B. 2017).

Due to the pollution of natural reservoirs, insufficient efficiency of existing water treatment technologies, and unsatisfactory condition of many water mains, a significant part of the population consume poor quality drinking water (Boyacioglu H. 2014). It should be noted that in a large part of the territory surface water and artesian water are characterized by slightly high or high mineralization degree (more than 1 g/dm^3) (Mirzavand M. et al. 2020, Radovenchyk, I. et al. 2021). In general, salinization is increasing due to the agriculture, resource extraction and industrial waste (Schuler M.S. et al. 2018, Grodzka-Lukaszewska M. et al. 2021). The situation is complicated by the uncontrolled discharge of huge volumes of wastewater and mine water (Mester T. et al. 2017). The total discharge of polluted wastewater into surface water bodies exceeds 66.0 million m^3/year . Excessive salinization of water resources leads to the deterioration of human health,

furthermore, the threat of biodiversity loss is also quite high (Vörösmarty C.J. et al. 2010). To reduce water scarcity, it is important to minimize freshwater intake and reduce wastewater discharges (Dharminder et al. 2019). In most cases, a difficult problem of water treatment is desalination of water with high mineralization and high water hardness.

The problem of water desalination is solved by using any of the known methods of water softening, desalination and deionization, such as reagent softening (Gomelya, M.D. et al. 2014), ion exchange (Luo T. et al. 2018), electrochemical methods (Trokhymenko G. et al. 2020) or pressure-driven membrane processes (Bodzek M. et al. 2019, Trus, I.M. et al. 2020). A common scientific problem is that all known methods of water desalination are accompanied by the formation of concentrated salt solutions (Trus, I.M. et al. 2021). The processing and disposal of such waste is a complex problem. Therefore, nowadays almost all technological processes of water desalination lead to a significant pollution of natural reservoirs with soluble mineral salts (Panagopoulos A. 2020).

Reverse osmosis filters are most often used for desalination of mineralized waters (Bodzek M. 2019). This process is characterized by relatively low energy consumption with high water purification efficiency (Lu H. et al. 2020, Hardikar et al. M. 2020). As a result of reverse osmosis desalination, highly mineralized concentrates are formed (Chen Q.-B. et al. 2019). The recycle process of such concentrates is very complex and resource-intensive, so such waste is simply disposed of (Trus, I.M. et al. 2019, Halysh V. et al. 2020). Therefore, to solve

this problem, the processes of ion exchange separation of these ions in the stages preceding the reverse osmosis desalination of water can be used.

The most characteristic anions of highly mineralized waters are chlorides, nitrates and sulfates. The use of an anion exchange resin Amberlite IRA 900 allows for the separation of chlorides and nitrates (Berbar, Y. et al. 2008). Today, reverse osmosis methods are preferred for purifying waters with a high content of chlorides and sulfates, (Mubita, T. et al. 2020). These anions can be preliminarily separated on the AV-17-8 anion exchange resin in Cl-form. During the electrochemical separation of chlorides and sulfates in the anode chamber, sulfuric acid is concentrated, and chlorides are oxidized and then released in the form of chlorine gas.

It is much more difficult to purify water that contains nitrates along with sulfates. It should be noted that the extraction of nitrates from water with low mineralization is a simple task (Rajca, M. 2012, Wiśniowska E. and Włodarczyk-Makuła M. 2020). Ion exchange is a fairly simple and reliable method that allows to effectively remove nitrates, reducing their concentration in water to acceptable levels. Ion resins are well regenerated with the solutions of sodium, potassium and ammonium compounds.

At high concentrations of chlorides and sulfates during their electrochemical separation a mixture of sulfuric and nitric acids will form, which is unsuitable for further use. Therefore, this issue needs to be addressed urgently. However, the processes of regeneration of ion exchangers and utilization of the resulting eluates are insufficiently studied.

Therefore, the aim of this work was to study the processes of effective separation of sulfates and nitrates depending on their concentrations in water and to develop a method of processing of eluates, which will allow their reuse to create low-waste water purification processes.

The objective of this work is to study the processes of ion exchange separation of sulfates and nitrates on the anion exchange resin AV-17-8 in NO_3^- form to develop effective methods of anion exchange resin regeneration considering possible directions of processing of the obtained eluates for reuse and to evaluate the prospect of ion exchange separation of anions from the water.

Experimental

The highly basic anion exchange resin AV-17-8 (DSTU 20301-74, TU Y 20.1-30166282-009: 2020 (Ukraine)) was used in the work. It was obtained by copolymerization of styrene and divinylbenzene with subsequent chloromethylation and amination of trimethylamine copolymer. Benzyltrimethylammonium groups capable of dissociation are the functional groups.

The processes of ion exchange separation of sulfates and nitrates were performed using the anion exchange resin AV-17-8 in NO_3^- form. A 20 cm³ ion exchange resin was placed in an ion exchange column which was 2 cm in diameter and 40 cm high. Reagent-grade sodium salts of nitrate and sulfate were added to tap water to prepare model solutions. During sorption, solutions containing sulfates in concentrations from 800 and 1500 mg/dm³ and nitrates from 0 to 1000 mg/dm³ were used. The consumption of solutions was 10–15 cm³/min. The sample

volume was 100–200 cm³. The content of sulfates and nitrates was determined in the samples during the sorption of sulfates.

To regenerate the anion exchange resin when converting it to the NO_3^- form, a 10% solution of sodium nitrate was used. The consumption of solutions was 1–5 cm³/min. The sample volume was 20 cm³. During the regeneration of the resin with a solution of sodium nitrate the content of sulfates in the solution was controlled. The used regeneration solution was treated with calcium nitrate, removing calcium sulfates from it. The filtrate was reused to regenerate the anion exchange resin.

The determination of sulfates was performed by spectrophotometric method with barium ions. The determination of nitrate concentration was performed by potentiometric method using an ion-selective electrode.

The total exchange dynamic capacity, the exchange dynamic capacity before leakage and the degree of regeneration of the resin were calculated by the formula:

$$TDEC = \frac{\sum_{i=1}^n (C_{in} - C_i) \cdot V_s}{V_i} \quad (1)$$

$$DEC = \frac{\sum_{i=1}^n (C_{in} - C_i) \cdot V_s}{V_i} \quad (2)$$

$$Z = \frac{\sum_{i=1}^n M_d^i}{M_s} \quad (3)$$

Where:

C_{in} – initial concentration of ions in solution, mg-eq/dm³;

C_i – the concentration of ions in the i -th sample after sorption, mg-eq/dm³;

V_s – sample volume, cm³;

V_i – volume of resin, cm³;

M_d^i – the number of desorbed ions with the i -th breakdown of the regeneration solution, mg-eq/dm³;

M_s – the number of sorbed ions, mg-eq/dm³.

Results and discussion

At the first stage of the study, the efficiency of separation of sulfates and nitrates on the anion exchange resin AV-17-8 was investigated. To prevent water from entering the ions other than nitrates, the anion exchange resin was used in the NO_3^- form. It is known that in natural waters in some cases the content of nitrates reaches 100 mg/dm³, in concentrates of baromembrane desalination of water their concentrations exceed 1000 mg/dm³. The content of sulfates in mine waters reaches 800 mg/dm³, and sometimes higher values. Therefore, we used model solutions based on tap water from Kyiv, which contained nitrates in concentrations from 0 to 1000 mg/dm³ and sulfates from 800 to 1500 mg/dm³.

The lower the concentration of nitrate ions is, the better is the sorption of sulfates and the higher is the efficiency of their removal from aqueous solutions. The higher the concentration of nitrates is, the worse is the sorption of sulfate ions. That is, the capacity of the resin on sulfates decreases with increasing concentration of nitrates in the initial solution. At the initial stage of sorption on the anion exchange resin, sulfate retention occurs effectively and therefore in the first portions of the

filtrate the concentration of sulfate ions does not exceed the maximum permissible concentration (MPC).

At a concentration of sulfates of 800 mg/dm^3 in the absence of nitrates, the exchange dynamic capacity (DEC) of the anion exchange resin on the sulfates before leakage reached 920 mg-eq/dm^3 , the total exchange dynamic capacity (TDEC) reached 1750 mg-eq/dm^3 . At a nitrate concentration of 100 mg/dm^3 , the capacity of the anion exchange resin on the sulfates before leakage reached 500 mg-eq/dm^3 , whereas the total exchange dynamic capacity (TDEC) reached 1290 mg-eq/dm^3 . When increasing the concentration of nitrates in water, the selectivity of the anion exchange resin for sulfates decreased (Fig. 1a).

As the concentration of sulfates and nitrates in water increases, the efficiency of their separation decreases. At a concentration of sulfates of 1500 mg/dm^3 in the absence of nitrates, the capacity of the anion exchange resin on the sulfates before leakage reached 310 mg-eq/dm^3 , the total exchange dynamic capacity (TDEC) at these concentrations reached 1600 mg-eq/dm^3 . The increase of the concentration of nitrates to 100 mg/dm^3 leads to a decrease in the capacity of the anion exchanger for sulfates. At the same time, the capacity of the anion exchanger for sulfates before leakage decreased to 250 mg-eq/dm^3 , and the total exchange dynamic capacity (TDEC) to 1160 mg-eq/dm^3 (Fig. 1b).

From the above results it can be seen that at sulfate concentrations below 800 mg/dm^3 and at nitrate concentrations up to 100 mg/dm^3 the separation efficiency of these ions is sufficient. This is an important aspect for obtaining individual substances or products suitable for use in desalination of waters containing sulfates and nitrates.

In the technology of ion exchange water purification, anion exchange regeneration is extremely important. Due to its high efficiency, simplicity, versatility and availability, chemical regeneration has become widespread. Regeneration of the anion exchange resin in SO_4^{2-} form with a 10% solution of sodium nitrate is quite effective. In this case, at a consumption of regeneration solution of $5\text{--}10 \text{ cm}^3/\text{cm}^3$, the degree of desorption (Z) of sulfates reaches $70\text{--}97\%$ (Fig. 2).

In this case, the treatment of the first 5 combined samples of the regeneration solution containing sulfates at a concentration of 244.0 mg-eq/dm^3 and a solution of calcium nitrate, produced a precipitate of calcium sulfate. The degree of sulfate extraction was $89\text{--}95\%$ (Fig. 3).

Clarified by decantation and filtration, sulfate-purified solutions were used to regenerate the resin. The degree of regeneration (Z) of ion exchanger exceeded 92% , and the capacity of ion-exchanger for sulfate anions reached 1700 mg-eq/dm^3 (Fig. 4).

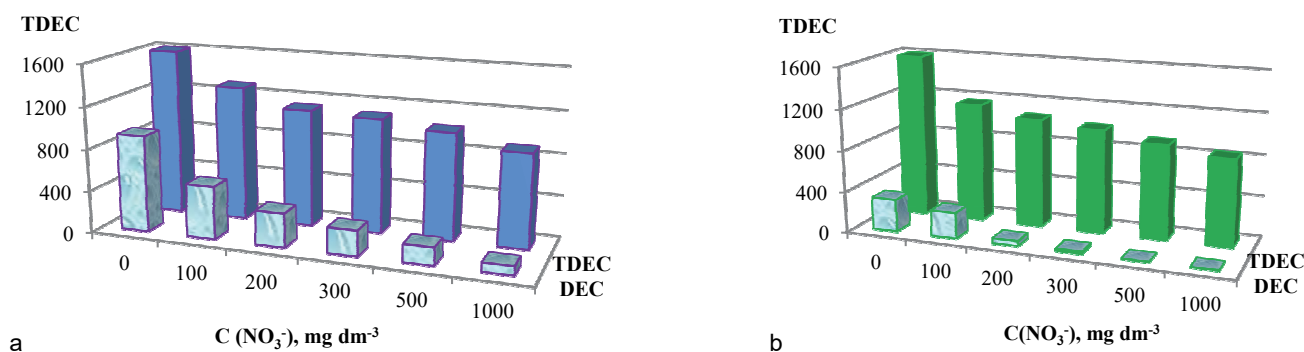


Fig. 1. The dependence of the exchange dynamic capacity of the anion exchange resin AV-17-8 before leakage (DEC) and its total dynamic exchange capacity (TDEC) for sulfates on the composition of the solution at a concentration of sulfates 800 mg/dm^3 (a), 1500 mg/dm^3 (b)

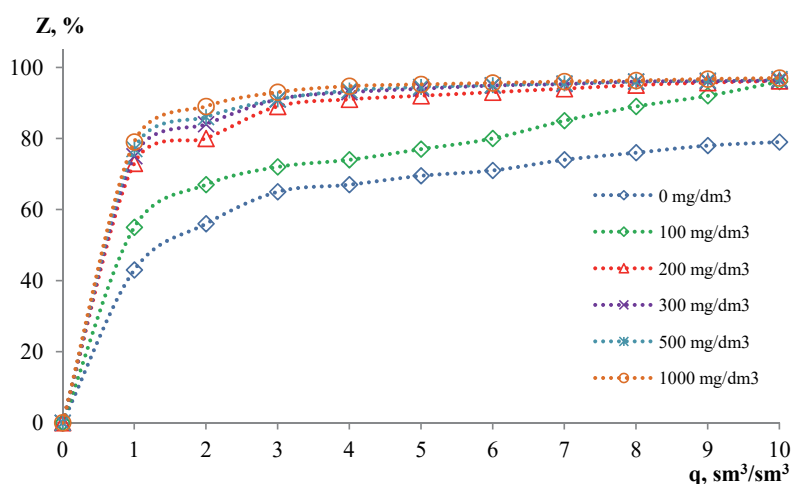


Fig. 2. The dependence of the degree of desorption (Z) of sulfate anions from the anion exchange resin AV-17-8 in mixed sulfate-nitrate form on the specific flow rate (q) of the regeneration solution (10% NaNO_3) depending on the concentration of nitrates

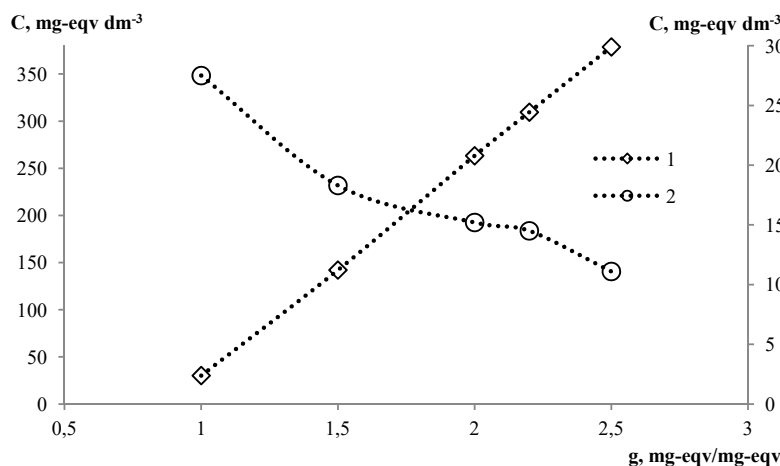


Fig. 3. The dependence of the residual concentration of calcium ions (1) and sulfates (2) on the consumption of a solution of $\text{Ca}(\text{NO}_3)_2$ (mg-eq $\text{Ca}(\text{NO}_3)_2$ per mg-eq SO_4^{2-}) in the reagent treatment of regeneration solutions

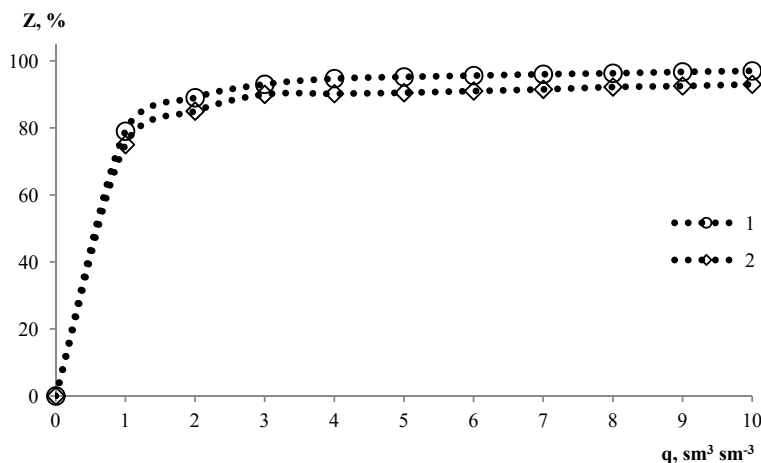


Fig. 4. Dependence of the degree of desorption (Z) of sulfate anions from the anion exchange resin AV-17-8 in mixed sulfate-nitrate form on the specific flow rate (q) of the regeneration solution during regeneration with fresh (1) and reagent-reduced (2) 10% NaNO_3

Thus, when using the anion exchanger AV-17-8 in NO_3 -form, sulfates can be removed from water in the form of gypsum. The resulting gypsum is compacted on a filter and used in the production of building materials. This allows creating low-waste water desalination technologies.

Conclusions

It was found that the efficiency of separation of nitrates and sulfates on the anion exchange resin AV-17-8 depends on the magnitude and ratio of their concentrations in water. Ion exchange separation of sulfates and nitrates on the anion exchange resin AV-17-8 in NO_3 form is effective at the concentrations of sulfates and nitrates up to 800 and 100 mg/dm^3 , respectively.

The conditions of anion exchange resin regeneration have been determined, a solution of 10% sodium nitrate should be used for effective desorption of sulfates. After precipitation from the used eluate of sulfates in the form of calcium sulfate, this solution is suitable for re-regeneration.

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Obiecująca metoda jonowymiennej separacji anionów przed odwróconą osmozą odsalania wód zmineralizowanych

Streszczenie: Celem pracy było opracowanie metody poprawy jakości oczyszczonej wody, obniżenia kosztów odczynników do regeneracji żywicy i stworzenia procesów niskoodpadowych. W pracy przedstawiono wyniki rozdziału jonowymiennego siarczanów i azotanów z użyciem żywicy anionowymiennej AB-17-8 w postaci NO₃. Skuteczność separacji anionów na wysoce zasadowej żywicy anionowymiennej AB-17-8 zależy od wielkości i stosunku ich stężeń w wodzie. Wykazano, że rozdział na żywicy anionowymiennej AB-17-8 jest skuteczny przy stężeniach siarczanów do 800 mg/dm³ i azotanów do 100 mg/dm³. Określono warunki regeneracji 10% żywicy anionowymiennej NaNO₃. Przeprowadzono odczynnikowe wytrącanie siarczanów z zużytego roztworu regeneracyjnego w postaci siarczanu wapnia. Osad siarczanu wapnia może być wykorzystany do produkcji materiałów budowlanych. Roztwór do regeneracji nadaje się do ponownego użycia. Opracowane wyniki pozwolą na wprowadzenie niskoodpadowej technologii odsalania wód wysokozmineralizowanych.