

ENVIRONMENTAL SAFETY OF CONSTRUCTION AND MUNICIPAL SERVICES

UDC 628.182

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SORPTION ORGANIC PURIFICATION OF RIVER FOLLOWING REAGENT COAGULATION

Statement of the problem. Organic matter is strictly limited in technological waters in many productions. Humic and fulvic acids, which dominate in natural waters, make it difficult to obtain highly pure water for nuclear and thermal power generation. Coagulation treatment enables the removal of only a part of a macromolecular organic matter. To determine sorption purification of clarified water low-base anion exchangers produced domestically were studied.

Results. In dynamic conditions industrial anionites EDE-10P and AN-31 and granulated products were tested. The influence of flow velocity on the working exchange capacity of anionites by anionam of strong mineral acids, and anionite sorption in different ionic form of the SC and FC river water was investigated.

Conclusions. It was found that demineralizing anionites absorb acid pellets, with non-granulated light water samples absorbing up to 80% up to 50% of fulvic acids. Granulated analogues of the tested anionites are less effectively absorbed by water humus. The tested anionites contribute to the purification of demineralized organic water.

Keywords: natural water, humic and fulvic acids, low-base anionites, sorption.

Introduction

A lot of industrial waters employ desalinated water which is obtained by conditioning natural waters by means of the ion exchange method, electrodialysis, reverse osmosis, etc. [1—5].

A lot of problems are known to be caused by a necessary removal of organic substances [1]. This stage of water treatment is always present in all water desalination technologies regardless of a further used demineralization method. Organic water impurities can have a range of negative impacts. Even the smallest amount of weakly dissociating organic electrolytes (carbon, humic, fulvic acids, etc.) prevent water with the resistivity $\rho \geq 18$ megaohm·cm from being obtained. [6] shows that ρ of a desalinated filter is determined not only by the quality of the original water but also a system of preliminary water treatment for the removal of humic acids.

These substances have a range of adverse effects on the quality of desalinated water: they increase the content of total organic carbon, reduce ρ , generate complex compounds of metal ions and are a source of potentially acid substances [1]. A particular note should be made that organic humic impurities do not only deteriorate the quality of deionate but also adversely affect ion-exchange materials employed in desalination setups [7, 8]. According to a lot of researchers, in the first stage filters ionites are “intoxicated” by humic acids.

Molecules of these compounds are thought to block the pores of desalination ionites thus reducing sorption characteristics of the latter [9—10]. Therefore ionites lose their exchange capacity while also reducing the longevity of filters, more frequent regenerations are thus needed which effectively results in more reagents to be used and more sewage water. As a result, there is worse economic performance of desalination setups and more environmental impacts to be addressed.

The removal of humic acids has not to date been addressed as part of water treatment problems. As a result of coagulation, there is a significant reduction in the amount of organic substances, sometimes it is a 60—80 % reduction. However, this is not enough to meet high requirements for the quality of desalinated water. Therefore, there is an ongoing search for synthetic anionites with a sufficient absorption activity in respect to organic combinations of natural waters.

1. Experimental determination of sorption properties of anionites

According to the authors' experience [11—12], anion-exchangers used for ion-exchange desalination setups absorb some organic substances from water which was preliminary treated using coagulation or sorption. I.e. desalination ionites designed for removing anions of miner-

al acids have a certain capacity in respect to organic water impurities. It would be reasonable to assess the contribution of these ionites into the removal of organic water impurities.

1.1. Characteristics of sorbents

The tested ion-exchange resins are industrially manufactured as well as samples of polycondensation anionites. They are anionites AH-31, ЭДЭ-10П and their analogues as well as ИА-n absorption anionites. All of the above sorbents are crucial for extra clear water. Resins of this type can be challenging to select in respect to organic substances: it is common knowledge that the less regular the structure of an ionite is and the more functional groups it has (phenylic, first and secondary amides, etc.), the more intense the absorption of organic impurities is [13].

The more complex and non-symmetrical an organic counter-ion being absorbed is, the harder it is to select ionites for it. This is one of the particular features of the absorption of organic ions: apart from the electrostatic interaction in the system “fixed ion-counterion”, there are other interactions of counter-ions with a polymer matrix of the ionite [13, 14].

Anionite ЭДЭ-10П has a high static exchange capacity (SEC) of anions of mineral acids: from 0.1 mole/l HCl to 2.3 mg-equiv/ml; dynamic exchange capacity (DEC) from 0.025 mole/l HCl to 1.1 mg-equiv/ml [15].

Anionite AH-31 is low-base and contains aliphatic secondary and tertiary amine groups. It is obtained by polycondensation of ammonia, polyethylene-polyamines and epichlorohydrin. Granulated analogue AH-31Г is different from the prototype because it has a regular spherical shape of the granules and a more elastic matrix and high osmotic stability [16].

Low-base anionites ИА-n were synthesized using meta phenylene diamin and resorcin (or phenol) at Nizhniy Tagil Department of Moscow Industrial Association Plastmassy (only ion-sorbent ИА-1 was obtained based on m-phenylene-diamin and resorcin).

In the development of this type of synthesization of anionites, it was necessary to introduce different ionogenic groups into a matrix in order to provide complete absorption of organic substances.

The main condition was to obtain a structure to ensure a deep penetration of large organic molecules with a molecular mass of 300—700 and more [17].

1.2. Study of ИА-n anionites

The physical and chemical properties of this group of anionites are not described, therefore we determined the structure of ИА-1 and ИА-3 anionites. Prior to the study, they were treated multiple times with a solution of acid and alkali to remove impurities that did not participate in polycondensation during the synthesis. After resin aliquots were washed off reagents and contaminating impurities, they were transformed into salts, i.e. Cl. In order to prevent hydrolysis of ionogenic groups, a final washing was performed using acetone followed by the drying at the temperature of 105 °C till the constant mass. Ground to fine powder, the sample was mixed with spectrally clean KBr and again ground in an agathic mortar and pressed into pills. The spectra were registered on a spectrophotometer Specord-U 25 (Fig. 1).

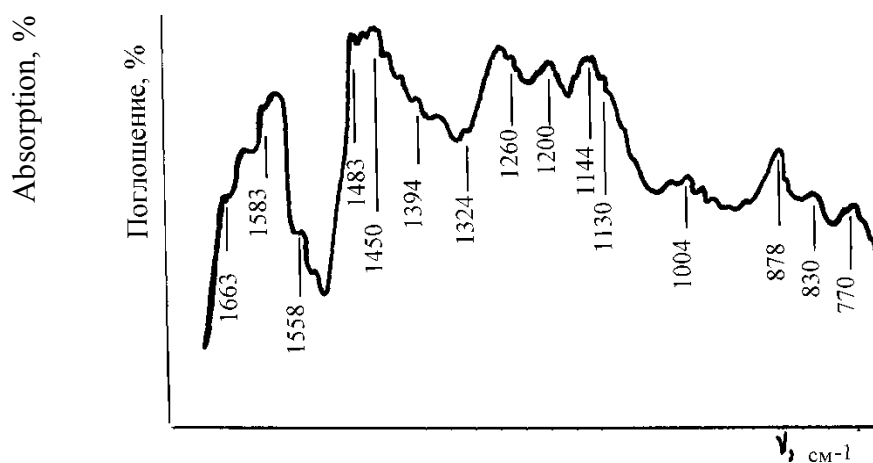


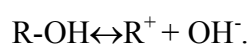
Fig. 1. Infrared spectrum of ИА-1 anionite

In this infrared spectrum there are absorption lines, which means there are out-of-plane deformation oscillations of CH-groups of a benzene ring in varying displacement degrees: 770 and 830 cm^{-1} as well as valency oscillations C = C of a benzene ring and deformation oscillations of CH_2 -groups (1490 and 1450 cm^{-1}). The lines at 1130 and 1324 cm^{-1} are superpositions of the valency oscillations C-O and plane deformation oscillations of OH alcohol groups. The line at 1200 cm^{-1} definitely indicates there are phenols in the sample. The absorption lines 1663, 1583 and 1144 cm^{-1} are results of the ions in the primary amine groups of the amines. In 1660 and 1540 cm^{-1} range monosubstituted amines are absorbed. Besides, in 1625—1710 range (the average one is ~1660) cm^{-1} dual substituted amines are absorbed. Primary amines have absorption lines in the range of 1560—1640, 1250—1350, 1100—1200, 1030—1120, 620—910 cm^{-1} [18]. Infrared spectrum of ИА-3 anionite is similar to that presented in Fig. 1

of ИА-1 spectrum. Therefore there are reasons to assume that these anionites are low-base as according to the infrared spectrum, the anionite being tested has primary amine groups.

This was proved by ionization constants of ionogenic groups of the sorbent. Their ionization capacity in the ionite is unknown. The main method for identifying their basicity is potentiometric titration. The ionization constants of functional groups makes the type of anionite more accurate and predict the range pH where there can be ion-exchange sorption of humic (HA) and fulvic acids (FA). pK_a was computed using the Henderson–Hasselbalch equation [13].

The ionization of the anionite is given by the equation



In the balance condition, the ionization constant of the anionite is

$$K_\alpha = \frac{[R^+][OH^-]}{[ROH]}.$$

Taking the logarithm and changing the sign to the opposite ones results in the expression:

$$-\lg K_\alpha = -\lg [R^+] - \lg [OH^-] + \lg [ROH].$$

Let us denote $-\lg K_\alpha = pK_\alpha$; $-\lg [OH^-] = pOH$.

Then for the anionite

$$pK_\alpha = -\lg [R^+] + pOH + \lg [ROH] = pOH + \lg \frac{[ROH]}{[R^+]}. \quad (1)$$

At the initial moment of time when there are only OH^- -groups in the ionite, they are assumed to equal 1, i.e. $[ROH] = 1$. In water when with H^+ -ions there is dissociation of anionites with $[ROH]$ reducing and $[R^+]$ increasing.

The number of functional groups without OH^- -ions equals the degree of ionization, i.e. $[R^+] = \alpha$. Then the remainder of $[ROH]$ in the sample is $(1-\alpha)$. Inserting the equation $(1-\alpha)$ into the equation (1), we have the following for the anionite

$$pK_\alpha = pOH + \lg \frac{1-\alpha}{\alpha}, \quad pOH = pK_\alpha + \lg \frac{1-\alpha}{\alpha}. \quad (2)$$

This expression was used to compute pK_α of low-base anionites. According to the equation (2), $pK_\alpha = pOH$ in the degree of ionization $\alpha = 0.5$, i.e. during a 50%-absorption of the ionite by chloride ions. As $pH = 14 - pOH$, the initial ionization constants of ИА-n anionites thus equals $pK = 14 - pH$. pK_α obtained using this method is an apparent ionization constant.

Equation (2) is the equation of the straight line which cuts off the line at Y-axis. The value of the line yields pK_a of the anionite in the neutralization degree $\alpha = 0$. This corresponds to the condition of this ionite at the beginning of titration. This is a more objective value to be used for the evaluation of the acid-base function of a titratable object as pK_a depends on the degree of neutralization of active groups.

Titration of anionites in hydroxide ion shape was performed using a solution $0.1 \text{ mole/dm}^3 \text{ HCl}$ using the method of a range of samples. The samples of a swollen anionite (2.0000 g each) were placed in some of the dry flasks of 50 cm^3 after water was separated by means of centrifugation. Each flask was injected with 50 cm^3 of the solution $0.1 \text{ mole/dm}^3 \text{ KCl}$. A portion of the acid was added into the mixture with the portion being increased by 0.1 cm^3 as a new test starts. The flasks were sealed with corks with two tubes. Through one of them argon cleared of CO_2 was administered for 1—2 minutes and it was extracted from the second one. Filling the flask with an inert gas in this manner prevented any contact of its content with the air. Tightly sealed flasks were stored at room temperature (20 ± 1) $^\circ\text{C}$ for 14 days. The solution was then decanted straight into the measurement cell of the ionometer in order to measure pH. An example of the titration curves of the anionite in the functional coordinates is shown in Fig. 2. They are slowly descending curves (Fig. 2a) with no maximums. Such curves are typical of ionites with one type of functional groups with a small ionization constant. In order to compute the mean pK_a , a graph dependence $pOH - \lg[(1-\alpha)/\alpha]$ (Fig. 2b) was used, which means that at $\alpha = 0.5$ an apparent ionization constant is about 7.8.

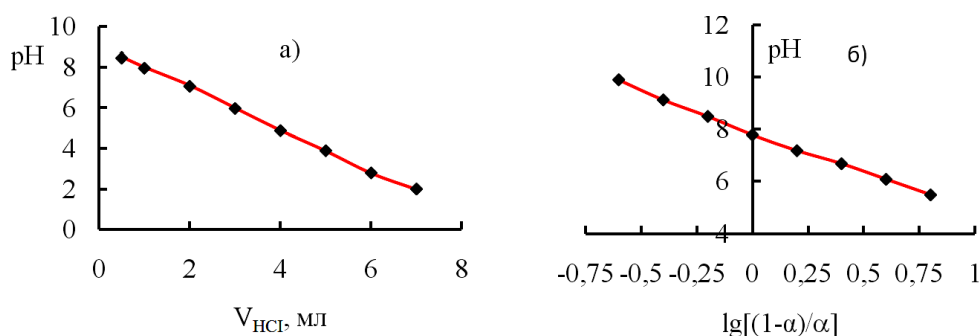


Fig. 2. Potentiometry curves of of low-base anionite ИА-1 in functional coordinates

Anionite ИА-3 is characterized by similar infrared spectra and potentiometry curves. Therefore, according to the obtained data, the conclusion can be made that ИА-1 and ИА-3 anionites are monofunctional low-base anionites.

2. Study of the sorptional capacity of anionites

The research was carried out using river waters preliminary coagulated by means of aluminium sulfate. It was treated with 10 litre portions. As was found in [1], sorption of organic substances using anionites is more efficient on ionites of acidulous solutions, after the coagulation clarified water was passed through a cationite filter in the hydrogen form (R-H) where the metal cations were removed, e.g. according to the reactions $R-H + NaCl \leftrightarrow R-Na + HCl$.

The flow rate was maintained (10 ± 1) m/h. The height of the anionite layer was 30—35 cm, the resin loading was 100 ml (AH-31Г — 65 ml). The filtrate was chosen in 1 litre fractions and permanganate oxidation in ten volumes of water treated with a volume of anionite. From 350 (through AH-31Г) to 420 (through the remaining anionites) volumes of water were passed through.

The efficiency of sorption using granulated anionite samples is indicated in Fig.3. The comparison of the motion of the curves indicates that the efficiency of their influence on the quality of water is almost identical. The same goes for the ratio of non-granulated samples of AH-31 and ЭДЭ-10П anionites as well as a low-base ion sorbent ИА-1. The histogram (Fig. 4) is indicative of that.

The following filter cycles were performed in late September. The quality of water in spring and summer time was different due to permanganate oxidation. So, in May on average it was 15 mg O_2 /l and 9.5 mg O_2 /l in June. Note that there was little difference in the content of humic and fulvic acids: 230 and 225 mkg/l of HA and 12150 and 13500 mkg/l of FA respectively.

In September when the oxidation is lower (7.2 mg O_2 /l), the concentration of HA rises up to 440 mkg/l and up to 15200 mkg/l for FA. This ratio of the oxidation and humic acid concentration means that in spring and summer there are a lot of organic substances in water which are readily oxidated with potassium permanganate. They are fewer of them as autumn comes and therefore permanganate oxidation drops.

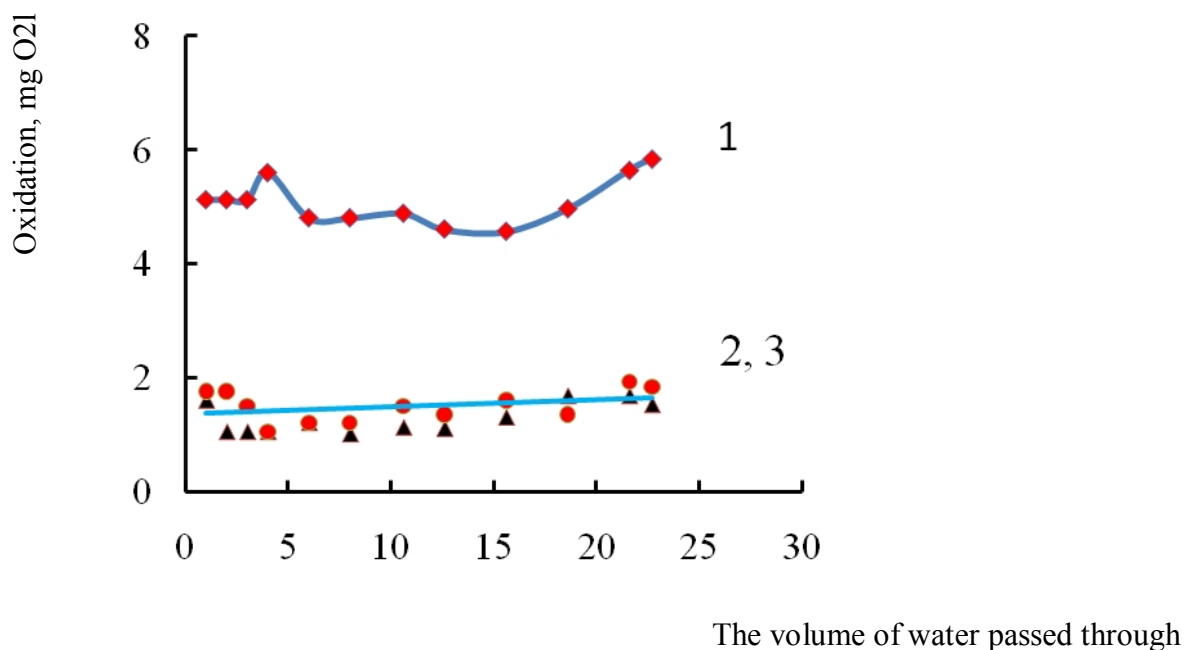


Fig. 3. Oxidation of river waters before (1) and after the filtration through granulated AH-31Г and ЭДЭ-10ПГ anionites (2,3)

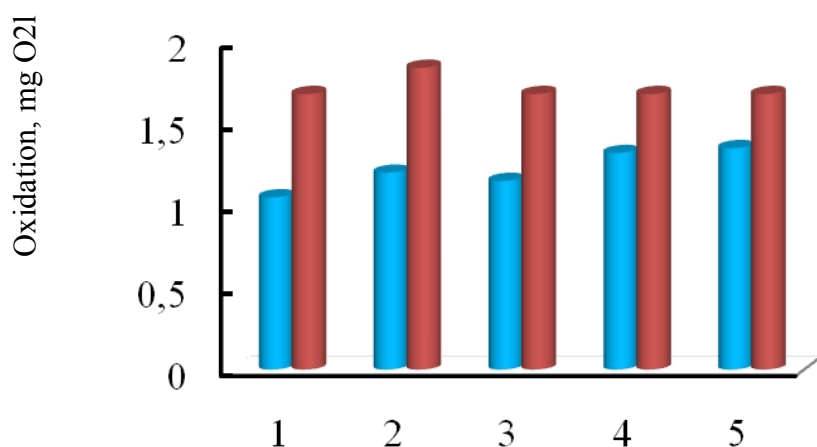


Fig. 4. Minimum and maximum permanaganate oxidation of coagulated water passed through anionites: 1 — AH-31; 2 — AH-31Г; 3 — ЭДЭ-10ПГ; 4 — ЭДЭ-10П; 5 — ИА-1

The average oxidation of the filtrate after the anionites was ~ 1.8 mg O₂/l (Fig. 4), i.e. it was still high with the requirement for desalinated water being 0.3—0.5 mg O₂/l. Therefore in order to make water treatment more efficient, the schemes were tested which combined sorbent ИА-1 with desalinating anionites. Besides, the rate of filtration was down from 10 to 7 m/h since kinetic characteristics of ionites as more organic ions are absorbed improve when there is more contact in the system “sorbent-sorbate” [18, 19]. For the experiment 100 litres of water was coagulated with the oxidation dropping from 7.25 to 3.66 mg O₂/l, i.e. it was less effi-

cient (in the total of 50 %), which is typical of water in the autumn-winter period [1, 11]. The results of the water analysis are summarized in the Table.

Table

Content of organic substances in the filtrate after the anionites

Type of water treatment	Oxidation, mg O ₂ /l	Humic acids, mkg/l	Fumic acids, mkg/l
Raw water	7.25	440	15200
Clarified water	3.66	120	3500
After ИА-1 ion sorbent	1.84	64	1350
After АН-31Г anionite	1.62	56	1075
After АН-31 anionite	1.72	16	600
After ЭДЭ-10ПГ anionite	1.65	48	750
After ЭДЭ-10П anionite	1.76	13	550

The data suggests that while there is little difference between the oxidations of water passed through the systems of anionites, the concentrations of the remaining humic and fulvic acids are significantly different. Note a high efficiency of the sorption using ЭДЭ-10П anionites for humic as well as fulvic acids. This is because the ionite contains up to 20 % of highly ionized groups of a quaternary ammonia compound [15] with the ionization constant of about 1—2 [20]. Therefore it can sorb such weak organic electrolytes as humic and fulvic acids not only due to physical absorption [13, 14] but also the ion-exchange mechanism.

The results suggest that in case there are high requirements for desalinated water, non-granulated anionites can be used as an extra stage of water conditioning during its demineralization. Therefore in the operation of a filter with a polyfunctional anion exchanger ЭДЭ-10П even in the desalination mode water with a lower HA and FA content is expected.

Desalinating anionites in ion-exchange setups are used in OH-form. They become salts during their further operation. There is an obvious increase in the content of organic impurities as the

solution is passed through. This typical movement of the output curve is shown in Fig.5 (curve 3) for ЭДЭ-10П anionite.

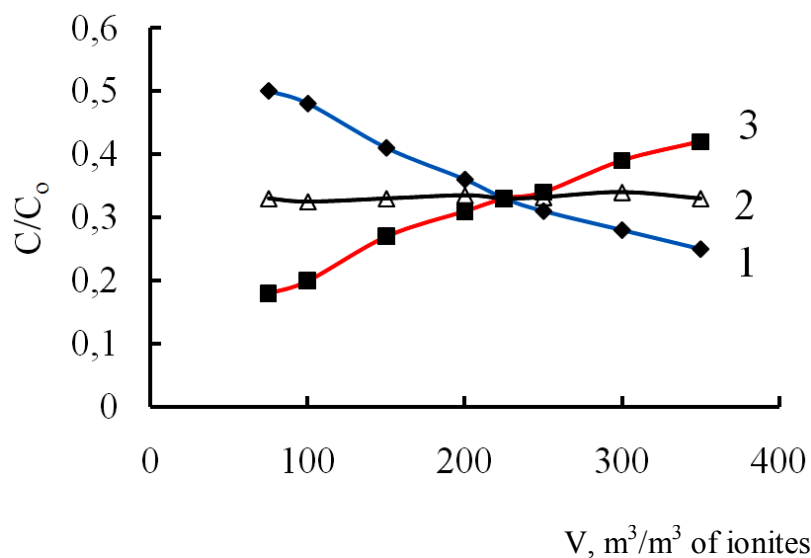


Fig. 5. Output curves of anionite sorption of FA in dynamic conditions:
1. AH-31; 2. AH-31 + ЭДЭ-10П; 3. ЭДЭ-10П

It is obvious that 15 % of fulvic acids “slips through” at the start of a filter cycle but it goes this figure goes up to 40 % of its initial content after 350 water volumes are passed through. At the same time, about 50 % of fulvic acids slips through AH-31 anionite but only 20 % of it does by the time 350 water volumes have been passed through.

There is an explanation for that. Ionogenic groups of a low-base anionite as they are treated with strong acid anions of non-dissociated OH-form become salts and ionized. As a result, counter-ions of the functional groups are hydrated, which causes an increase in the moisture capacity of the granules and their swelling capacity as well. This makes it easier for FA to penetrate deeper anionite pores. In addition, ion-exchange of FA sorption using ionized ionogenic groups of AH-31 anionite becomes possible. As a result, there is a sorption increase and less FA slips through into the filtrate (Fig. 5, curve 1).

It was assumed that the combination of these ionites would result in a more stable quality of water since as anionites are treated with mineral anions, a drop in the sorption of organic impurities by ЭДЭ-10П anionites will be made up for by an increasing sorption of the substances by AH-31 anionites, which was found to be true. The mixture of AH-31 and ЭДЭ-10П anionites with the volume ratio 1:1 was tested not only in the laboratory on a model solution of fulvic acids but also in OH-anionite industrial filter on river waters. The content of FA in the water after the filter with a mixed layer of the anionites is almost stable (Fig. 5, curve 2).

Therefore, at the start of a filter cycle AH-31 passes through about 50 % of FA and ЭДЭ-10П does only 20 % and at the end of the operation it is 20 and 40 % respectively. I.e. each certain anionite does not contribute to the overall stable quality of water. After the mixing of two types of OH-anionites, the quality of the filtrate was maintained, which is significant for deep water desalination.

Conclusions

Desalinating anionites are shown to contribute to the removal of organic substances from desalinated water of easily oxidized as well as not easily oxidized highly molecular humic and fulvic acids in a certain way. This has been revealed for the first time and distinguished according to the type of humic acids. ЭДЭ-10П anionite on an epichlorohydrin matrix has a higher sorption capacity as it contains functional groups of varying degrees of ionization, which gives rise to a double absorption mechanism which includes physical absorption and ion exchange. Anionites of varying basicity need to be mixed for a stable quality of the filtrate.

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