COAGULATION-AND-SORPTION PURIFICATION OF WATER FROM HUMIC SUBSTANCES

Background. Deep desalination of natural waters involves considerable difficulties associated with removal of humic and fulvic acids. Application of activated carbons for this purpose is inefficient. Besides, thermal regeneration of such a sorbent outside the filter is required.

Results. Synthetic porous anion exchangers capable of not only absorbing organic impurities but also desorbing on load treatment with alkali in the same filter, appeared to be perspective. Obtained optimal parameters of anion exchanger operation were corroborated in industrial desalting plants.

Conclusion. It is shown that removal of humic acids by sorption is more profitable than removal by coagulation in the context of environmental protection. In addition, the possibility of use of regenerators of desalting anion filters for anionite-sorbent treatment was proved to be real.

Keywords: natural waters, humic acids, fulvic acids, coagulation, sorption.

Introduction

Obtaining high-resistance desalinated water for precision manufacturing is not possible without organic substances removal [1]. This problem is of great importance to other kinds of manufacturing as well [2].

The analysis of water from various sources and examination of the test results of an ion-exchange water demineralization plant operation allow us to conclude that high-resistivity
filtrate with specific electric resistance of $\rho > 10$ Mohm per cm can be obtained with water coloration up to 5 degrees of the chrome cobalt scale and with oxidability not above $2.0...2.5$ mg $O_2$/dm$^3$ [3].

It should be remembered that the content of fulvic acids in natural waters is 10…30 times higher than that of humic acids [4]. Thus, it’s mainly fulvic acids that we find in desalinated water [5]. Their removal during water supply into demineralizing filters is determined by the need to protect anionites and ion-exchange membranes from the contamination by humic substances.

Hydrochemical characteristics of European Russia river waters oxidability help to reach the conclusion that before desalination processes with the help of the ion-exchange or membrane methods, all of them require preliminary removal of organic substances [4]. The choice of this or that desalination method is governed by the deionate quality requirements and the amount of impurities in an initial water sample.

As physical and chemical properties of humic and fulvic acids were further studies and the absorption laws of the latter by anionites of various types were found thus providing an extensive experience in an ion-exchange plant operation, the process of water conditioning was upgraded.

1. Humic acids removal by the combination of coagulation and sorption

At the first research stage [5], it was found that among domestically produced sorbents tested the most promising are low-based phenol condensation anionites of Type Ionosorbent ИА. Not only do they possess high sorption and kinetic characteristics but they are capable of desorbing the substances absorbed by alkali solutions (0.25…0.5 mole/dm$^3$). This fact enabled the application of alkali reclams used after the regeneration of desalinating OH-filters of ion-exchange plants.

Traditionally, a sorbent (usually activated carbon) used to be the “head” filter catching water organic impurities. It is on these grounds that a sorption filter with anionite ИА-1 was at the top of the scheme (Fig. 1). It included the following operations:

1) impurities coagulation by an aluminum sulfate (alumina) and water clarification in a mechanical filter with a two-layer loading;

2) sorption purification from organic substances in a filter with a porous anionite sorbent of organic substances ИА-1;
3) hydrogen ion polishing (metal ion removal) in a filter with a strong-acid cationite КУ-2-8 in H-form;

4) decarbonization of hydrogen ion polished water (CO₂ removal) in a degasifier by Rashig rings by air blowing with the calculation 20 m³/m³ of water;

5) OH-anion exchange of water for removal of strong acids anions and organic substances in a filter with anionite АН-31 in OH-form;

6) final water desalination of stage 1 of deionization by Step II in a filter of mixed action ФСД-II (cationite КУ-2-8 with anionite АВ-17-8 in a volume relationship 1:1.4).

Fig. 1. Basic technological diagram of lake water pre-preparation and desalination:
1 — mechanical filter; 2 — porous ИА-1-С1 anionite filter; 3 — N-cationite filter with cationite КУ-2-8; 4 — decarbonator; 5 — АН-31-ОН anionite filter; 6 — mixed action filter (ФСД-ИI); 7 — collecting tank for coagulator operating solution; 8 — collecting tank of a concentrated solution of a coagulator; 9 — filter for clarification of a coagulator solution; 10 — tank for dissolving a coagulator

Anionite ИА-1 was used in С1-form. This provided for its higher organic capacity in relation to humic and fulvic acids and prevented the formation of calcium and magnesium hydroxide resin in a layer.
In a diagram (see Fig. 1) it is shown that a coagulation area consists of a solution tank of an alumina coagulator (10), a filter for clarification of a concentrated alumina solution $\text{Al}_2(\text{SO}_4)_3$ (9), collector tank of its concentrated solution (8), an injection tank of the operating coagulator solution (7). The diagram does not present a dosing pump of a coagulator solution, shut-off apparatus, lines of pressure air supply into a supply tank, manometers, indicators of a solution level in the tanks, etc. There are also no containers for solution making and storage of regenerates solutions and scourage forming in the filter regeneration process. The technology for obtaining high-resistance desalinated water according to this scheme with the use of a synthetical porous anionite as a sorbent of organic substances was introduced on lake water desalination plant.

The organic substance content was decreased, on the average, by $50\%$ (in oxidability). $40...50\%$ of the amount of impurities left of anionite was sorbed, i. e. the total purification effect was $70...75\%$. The water quality by some parameters after 2, 15 and 230 hours of a sorbent-filter operation is given in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Lake water quality index</th>
<th>Initial water</th>
<th>Filter operating period, h</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Oxidability, mg $\text{O}_2/\text{dm}^3$</td>
<td>5.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Humic acids, mkg/$\text{dm}^3$</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>Fulvic acids, mkg/$\text{dm}^3$</td>
<td>6500</td>
<td>1050</td>
</tr>
<tr>
<td>Esters, mkg-equiv/$\text{dm}^3$</td>
<td>100</td>
<td>110</td>
</tr>
<tr>
<td>Water purified, $\text{m}^3/\text{m}^3$</td>
<td>-</td>
<td>7</td>
</tr>
</tbody>
</table>

Using the data from Table 1, we can conclude that the additive effect of preliminary water purification from organic substances in a criterion “permanganate oxidability” is $\sim 72\%$ even at the end of the filtration cycle when $770\, \text{m}^3/\text{m}^3$ of water was purified. By this moment, breakthrough of humic and fulvic acids into a filtrate reached 70 and 42%, i. e. humic acids are less effectively captured by an anionite sorbent. This is fairly explainable, since, in case of the humic acid, a
steric factor comes into play and the presence of a lower quantity of carboxyl groups in its molecule which are also less ionized than COOH-groups in a fulvic acid molecule. An ion-exchange component is thus lower during humic acid sorption than in case of fulvic acids.

With a slight increase in oxidability (after 15 and 230 hours of filter operation) breakthrough of fulvic acids become twice as large. This was revealed by the differential control of water quality in terms of humic and fulvic acids content. Some technological indicators of lake water desalination plant performance with a preliminary purification from organic substances of humus nature by the combination of coagulation and sorption after a year of operation are given in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Indicator name</th>
<th>Operational data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific water electrical conductivity $\rho$, MOhm-cm</td>
<td>5…15</td>
</tr>
<tr>
<td>Water permanganate oxidability, mg O$_2$/dm$^3$</td>
<td>0.7…1.0</td>
</tr>
<tr>
<td>Water volume treated by 1 m$^3$ loading of:</td>
<td></td>
</tr>
<tr>
<td>- a mechanical filter</td>
<td>65</td>
</tr>
<tr>
<td>- a cationite filter with cationite КУ-2-8</td>
<td>300</td>
</tr>
<tr>
<td>- an anionite ИА-1 filtera</td>
<td>600</td>
</tr>
<tr>
<td>- an anionite АН-31 filter</td>
<td>500</td>
</tr>
<tr>
<td>- a mixed action filter ФСД-II</td>
<td>370</td>
</tr>
</tbody>
</table>

Thus a filter-sorbent being placed before a cationite column of 1 m$^3$, anionite ИА-1 purifies an average 600 m$^3$ of coagulated and clarified lake water of the quantity presented in Table 1.

2. Sorption removal of humic acids from water by a porous anionite in a monolayer

Coagulation treatment involves water enrichment by strong mineral acids aniones which are to be removed during further desalination processes. So, in case of lake water, with the content of hydrochloric and sulfuric acid aniones 2.2…2.4 mmole-equiv/dm$^3$ and an average 1 mmole-equiv/dm$^3$ of Al$_2$(SO$_4$)$_3$, the loading on OH-anionite filter in the quantity of aniones removed grows almost by 50 %.
Thus, alkali expense and the volume of alkaline sewage waters during coagulation purification of the given water also grow by 50%, which can be prevented provided organic substances are not removed by coagulation but by sorption by anionites. This is unacceptable with a moderate organic substance content in an initial water sample (up to 5…6 mg O₂/dm³) or in case of low water quality requirements.

Excluding a coagulation stage of water treatment from the technology with no effect to water quality in organic substance content become possible after the analysis of the laws of humic substances sorption by ionites revealed that it’s mostly a solution pH that affects its sorption capacity rather than an ionic shape or granulometric composition of anionite. Organic capacity of an anionite rapidly increases in the acid environment. It is also found that the positive effect can also be achieved by warming up water [3].

Conducted in a laboratory environment, six cycles of organic substance sorption-desorption from water with oxidability 5.4…6.7 mg O₂/dm³ according to the scheme: КУ-2-8-Н→ИА-1-C1 on a test bench with productivity per 15 dm³/h showed the stability in porous anionite performance decreasing the oxidability by up to 0.8…1.0 mg O₂/dm³ at the flow speed of 7 m/h.

The influence of this method of water preparation on the deionate quality was also studied on a test bench plant according to the full scheme КУ-2-8→ИА-1→АН-31→ФСД-II with the resin volume in the columns being 200 cm³ and ionite layer height 40…45 cm. The flow speed through cationite КУ-2-8 and anionite АН-31 is 15 m/h, ФСД-II is 20 m/h and ИА-1 is 7 m/h. Natural water simulate quantity (prepared on artesian water) was as follows: 400 mkg/dm³ of humic acid, 10000 mkg/dm³ of fulvic acid with oxidability 8.3 mg O₂/dm³. A fresh ИА-1 anionite absorbed up to 80% of organic substances. The desalinated water (deionate) oxidability was 0.4…0.9 mg O₂/dm³ and specific electrical resistance ρ from 4 to 10 Ωm·cm, which was in agreement with the production requirements.

It was then proved in the production environment during a purification process of lake water on a pilot plant with the productivity 0.36 m³/day that there is a possibility in principle to remove humic acids by the sorption methods only. Before hydrogen ion polishing the water was warmed up to 25…30 °C. The filters contained 600 cm³ of ionites each. A cationite column was shut off if the oxidability of hydrogen ion polished water fell by 0.1 mmole/dm³, the same was done to the anionic column with АН-31 during Cl-iones breakthrough and to the
anionite column with a НА-1 sorbent after 1000 volumes of hydrogen ion polished water were put through the loading volume and lastly to ФСД-ИІ as the value $\rho$ fell to 1 MOhm-cm.

300 litres of water were put through a porous anionite. The water oxidability fluctuated in a range 4.9…5.5 mg $O_2$/dm$^3$ through the course of the experiment. In Fig. 2 there is an illustration of water oxidability change according to the treatment stages on the specific plant. A porous anionite absorbed up to 80 % of organic substances from ware under these circumstances as well. They decreased by twice their original number after АН-31 anionite.

ΦСД-ИІ was found to play a significant role in water purification from organic substances. As a result, we obtained water with the oxidability value less than 1.0 mg $O_2$/dm$^3$ with values $\rho \geq 1$ MOhm-cm. Multiple cycles of water desalination conducted according to a new scheme where an adsorber is placed after N-cationite showed the stability of the desalinated filtrate quality.

On the basis of laboratory modelling results and production bench tests, the method elaborated has been introduced on a production plant (Fig. 3).

It should be noted that excluding coagulation allowed to increase the desalination plant productivity by 1.5 times on the same equipment which there was no way of doing during straight-flow coagulation, since the time for coagulation would not be enough and a sediment
Al (OH)$_3$ could form in water on leaving the filter. Besides, the absence of coagulation knot in many ways simplified the technology and instrumental design of the plant, which is proved by the comparison of the diagrams in Fig. 1 and 3.

![Diagram](image)

**Fig. 3.** Basic technological diagram of sorption pre-preparation and desalination of lake water on a plant with the productivity 1.5 m$^3$/h:

1 — N-cationite filter; 2 — porous ИА-1-C1 anionite filter; 3 — decarbonator; 4 — ОН anionite АН-31 filter; 5 — ФСД-II

3. **Acid consumption calculation for anionite activation**

The application of anionite in the salt form (in contrast to the hydroxyl one) improves the filtrate quality but it also requires acid consumption for substituting OH-iones in anionite. Under operating conditions, it was revealed that in order to convert ИА-1 anionite into a C1-form, a lot of acid is needed, since it has a large complete exchange capacity (up to 6 Mmole-equiv/g). Besides, after anionite saturation with C1-iones (we call this process activation), the filter had to be washed from the acid excess, which increased the sewage water volume.

It appeared necessary to find out a minimum converting degree in ИА-1 anionite adsorber from OH-form into the salt form when its high sorption activity is already reached but washing away acid is not needed yet. As this took place, acid consumption decreased, while solution concentration grew for the reduction of its volume in order to decrease the general filter regeneration time and reduce the sewage water volume. The filtrate quality in relation to ИА-1 ion-exchange activation mode is illustrated in Table 3.
Table 3

The filtrate quality after the application of ИА-1 anionite in relation to the acid consumption for its activation

<table>
<thead>
<tr>
<th>Indicators</th>
<th>HC1concentration, mole/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Acid solution volume, m³/m³</td>
<td>2</td>
</tr>
<tr>
<td>Water consumption on cleaning, m³/m³</td>
<td>20…25</td>
</tr>
<tr>
<td>Anionite ion form</td>
<td>OH- Cl</td>
</tr>
<tr>
<td>Cleaning efficiency, %</td>
<td>72…78</td>
</tr>
<tr>
<td>Filtrate oxidability, mg×O₂/dm³</td>
<td>1.9…2.1</td>
</tr>
</tbody>
</table>

The data from Table 3 suggests that with acid solution consumption with the concentration 2 mole/dm³ at the rate of 0.125 m³ per 1 m³ of anionite, there is no need to wash HC1 from it. The quality of water purified stays the same as while converting all the anionite load into C1-form. The reason is that even a low layer of anionite converted into the salt form provides for a high efficiency of impurities sorption.

As acid hydrogen ion polished water is further put through, anionite lower layers are converted into the salt form by strong acid anions according to the following reaction

\[ R-OH + HCl \rightarrow R-Cl + H_2O, \]

where \( R \) is anionite matrix.

The laboratory test results are proved by longtime commercial operation of lake water desalination plant with the productivity of 1.5 m³/h with sorption roughing on ИА-1 anionite OH-C1 form (Fig. 4). It is clear that organic substance content in water after filtration through ИА-1 anionite falls by 2…2.5 times, while the level of production requirements is reached (~1 mg O₂/dm³) in combination with AH-31 anionite in the oxidability value.

Thus, with moderate oxidability of river water in a discovered mode of sorption-desorption, porous ИА-1 anionite and its ИА-2 analog provide for a level of organic substance removal during further desalination process allowing to obtain a deionate meeting the production re-
requirements for semiconductors. Such water after being put through the final plant in a work station has the value of $\rho=18$ MOhm·cm.

![Graph showing oxidability change over time](image)

**Fig. 4.** Change in lake water oxidability (1) during filtration through HA-1 anionite in a combined in OH-C1-form (2) and OH-anionite AH-31 (3) in a commercial desalination plant with the productivity of 1.5 m$^3$/h

Obviously, either preliminary mechanical filtration or chemical coagulation is unavoidable with the presence of suspended matter in water and, as a result, its more dramatic contamination by organic substances. A mineral coagulant dose can be generally decreased by the application of synthetic flocculants, however, these substances are unacceptable in desalinated water. To ensure their absence in a filtrate, the latter should be dosed with a great accuracy in any specific case with the consideration of the content of impurities, which is a hard thing to do with the initial water quality changing (see curve 1 shape in Fig. 4).

4. Porous anionite application in a combined layer

Ways of the intensification of equipment and ionites operation are being sought in the world practice of ion-exchange water conditioning, the combination of strong — and week-acid cationites and strong- and week-based anionites among many [1].

For decreasing the number of filters in a plant and reducing the volume of the used ion exchange reactors, a possibility of the application of a filter performing two simultaneous functions, such as hydrogen ion polishing and organic substance sorption, was looked into.
For this purpose, a mixed action filter was designed and produced. Its charging consists of equal volumes of strong-acid КУ-2-8 cationite and porous ИА-1 (ИА-n) anionite. The filter suggested with this kind of charging was called “ФСД-I”, since it takes part in the first stage of water desalination unlike the above mentioned ФСД-II, which is the second stage of desalination, charged with highly ionized КУ-2-8 and АВ-17-8 ionites.

ФСД-I was tested in Neva River water with oxidability of hydrogen ion polished water of 0.5 mmole-equiv/dm$^3$. It emerged that combined charging removes 20…25 % more of organic substances (in oxidability) than during a sequential water filtration through the same amount of cationite and anionite. Perhaps, the reason for more even distribution of water flow in a layer made up of various types of resins, i. e. anionite with irregular particles and granular-type resin.

According to a sorption front width (~15 cm) found earlier, a layer height in a filter should be no less than 135 cm in order to provide for efficient performance of ИА-1 anionite layer. The combined charging is of the same height but it contains twice as few resins than in individual filters with КУ2-8 cationites and ИА-1 anionite-sorbent. This filtration schemes thus allows to decrease the number of filters and ionite consumption without decreasing the water purification level (Fig. 5).

Fig. 5. Basic technological diagram of water desalination:
1 — ФСД-I; 2 — decarbonizer; 3 — ОН-anionite; 4 — ФСД- II
It is natural that in the season of spring and autumn flood with a large amount of suspended matter in water and thus with high turbidity and coloration coagulation is included before ФСД- I. In summertime, however, a sufficient purification height is provided by ФСД- I combined function and demineralizing filters ОН-anionite and ФСД-И.

5. Regeneration of a filter with mixed charging

The important stage of the filter with mixed charging operation is its regeneration which starts with splitting ionites into monolayers. It should be noted that although granulometric composition of both components was not altered, their complete splitting (with a cationite down) was accomplished with the intensity of the counterflow water supply being 8…10 dm$^3$/m$^2$·h which was found experimentally in a laboratory column with the same correlation of the diameter and layer height as in a production filter. The separation process was visually controlled through an eyeglass placed at the average drainage system level.

An ordinary demineralizing ФСД-И charged with highly ionized КУ-2-8 cationites and АВ-17-8 anionites after being split into alyers (with cationite below) regenerates by counter flow solutions. The acid solution is supplied into a layer with a cationite down through a lower drainage, while alkali solution is supplied in a downward direction through an upper drainage, i. e. towards each other, then they are brought out into the middle drainage placed at the boundary level of the resins.

Ionites are water-cleaned according to the same scheme [1]. However, with the application of this technology of ionite treatment in ФСД-И, porous anionite will be in inefficient ОН-form.

As a result of the filter regeneration by the method we suggested, anionite is in a salt ion form and besides, no fresh acid solution is needed for its activation. The diagram of the treatment of combined ion-exchange sorption ФСД- I filter charging is presented in Fig. 6.

As a porous anionite regenerant, 0.25…0.5 mole/dm$^3$ of caustic soda solution or treated alkali regenerate of ОН-anionite filter of the first stage of dasalination (АН-31). The layer washing off the alkali excess is done with raw water. Its result is controlled by phenolphthalein. Before ФСД-И filter regeneration, the charge mixture components should, however, be separated. With that purpose, water is supplied from below into ФСД-И filter and brought out through the upper drainage device. Ionites are separated in a water flow. Being heavier, the cationite is below and anionite, being light, is above.
At first a specified volume of the alkali solution is in a downward direction put through an anionite layer and is brought out through the middle drainage into the sewage system. Then ИА-1 anionite converted into OH-form is washed off the alkali excess and regeneration products with raw water. Then the acid solution is supplied into a cationite layer and is brought out through the middle drainage. The cationite layer is partially washed off the acid in a water flow. After that porous ИА-1 anionite in OH-form is mixed by compressed air with N-cationite whose layer still has some acid in it. Its excess is absorbed by the anionite and converted into a necessary ion form according to the reaction

\[ \text{R-OH} + \text{HCl} \rightarrow \text{R-Cl} + \text{H}_2\text{O} \]

while the cationite is “washed” off the acid excess. Finally, the filter is set for operation.

Hence the application of alkali regenerators of demineralizing filters for organic substance desorption out of porous anionite and its conversion into a salt form by the wastes of N-cationite filter regeneration excludes the consumption of fresh reagent solutions.

Besides, the application of anionite-sorbent in a mixture with a cationite in ФСД-I to a greater extent decreases the sewage water volume and reduces the water consumption for the plant’s needs.
Conclusions

1. Organic substances from natural waters with their high content (with the oxidability of 8…10 mg O_2/l) would be appropriate to remove by the combination of reagent coagulation and sorption if the desalinated water quality requirements are fairly high, say, in accordance with [6] for precision manufacturing. With a lower contamination of an initial water sample by the impurities of this kind, a sorption purification on a porous anionite in a salt form at 35…30 °C and pH 3…5 will suffice.

2. The quality and the volume of purified desalinated water has been significantly increased using the same equipment but considering the experimentally found laws of humic acid sorption by ИА-1 anionite.

3. The realization of two simultaneous processes, i.e. the removal of metals ions and organic substances in the same filter, allowed to simplify greatly the hardware design of the ion-exchange plant, decrease the number of filters by two units, reduce the reagent and water consumption on the ion-exchange plant’s needs by utilizing alkali and acid sewage waters from ion-exchange filters regeneration.

References


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