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Development of Scaling Reagent for Waters of Different Mineralization

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ABSTRACT
Membrane technologies are widely used for desalination of water. These technologies are environmentally friendly, economical, energy efficient and material efficient. In the absence of pre-treatment of water, the membrane is contaminated, which leads to an increase in the amount of concentrate formation. Discharge of mineralized water leads to physical and chemical pollution of water bodies. Dissolution and removal of these sediments is a complex issue, so the use of sediment inhibitors is important. The use of antiscalants allows to prolong the service life of membrane elements, which, in turn, will reduce the intake of fresh water and reduce the volume of wastewater. The efficiency of gipan as a reagent in the stabilization treatment of low-mineralized, highly mineralized waters at a temperature of 60°C was determined. The dependences of water stability on sediments on the chemical composition of water, inhibitor concentration and time of ultrasonic treatment of gipan were established.

Keywords: antiscalant, temperature, mineralized water, reverse osmosis, stabilizing effect, anti-scale effect.

INTRODUCTION

Providing the population with quality water is a global problem nowadays and needs an urgent solution (Cohen et al. 2017; Remeshevska et al. 2021, Trus^b and Gomelya, 2021). Reverse osmosis (RO) is one of the most widely used and highly efficient membrane desalination processes, which reduces water deficiency (Trus et al. 2019, Trus et al. 2020). Membrane technology has been used in desalination and wastewater treatment of various mineralization degree, including highly mineralized waters (Cho et al. 2016, Ghani et al. 2018). The main advantages of this process are simpleness of operation, smaller area, higher efficiency and lower consumption of chemicals compared to conventional technologies (Yelemanova et al. 2021; Trus et al. 2021, Trus^b et al. 2021). However, the widespread use of RO desalination processes is limited due to membrane contamination (Humoud et al. 2020, Wang & Lin, 2017). This leads to a decrease in the performance of the RO membrane, increased operating pressures, increased energy demand, deterioration of permeate quality and increased maintenance costs (Qu et al. 2020). Membrane contamination (fouling) can be caused by the formation of insoluble or poorly soluble inorganic substances ($CaSO_4$, $BaSO_4$, $CaCO_3$, CaF_2, SiO_2, Fe, Mn, Si compounds); organic substances of natural and artificial origin; sediments of biological origin (bacteria, algae and products of their vital activity); suspended particles and colloidal impurities (Laqbaqbi, M. et al. 2017, He, Z. et al. 2021, Ong, C.S. et al. 2016) (Fig. 1).

Inorganic pollution is a difficult problem due to the large number of total solutes in water (Rezaei et al. 2020, El-Dakkony et al. 2021). Various methods are used to reduce the risk of scale formation on the membrane (Fig. 2).

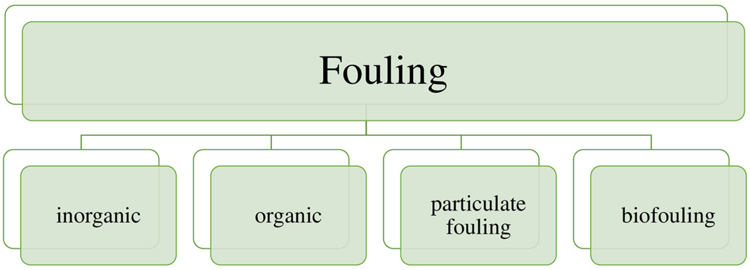

Figure 1. Types of fouling

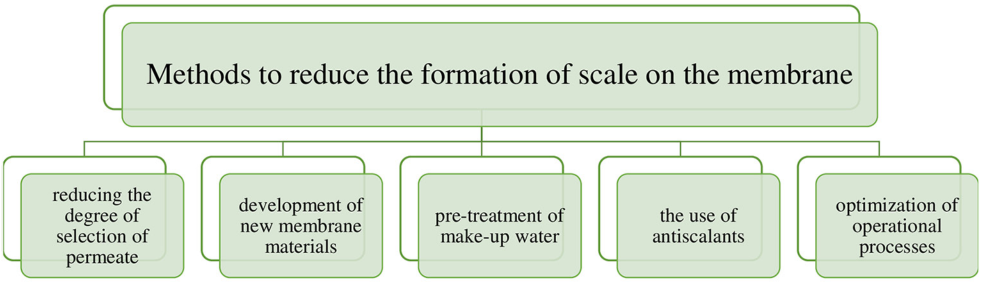

Figure 2. Methods to reduce the formation of scale on the membrane

Advances in materials science and membrane preparation processes provide new opportunities in the development of new generation membranes with better selectivity and antifouling ability (Du et al. 2018, Barbhuiya et al. 2021).

In the case of RO desalination of water, the degree of permeate selection is chosen so as to prevent the formation of sediment on the membrane. However, if the reduction in the degree of permeate selection does not prevent the formation of sediment, methods of pre-treatment of water or introduction into the stream of antiscalants are used. Pre-treatment of water with sulfuric acid to adjust the pH was effective in inhibiting the formation of calcium carbonate deposition. However, the addition of acid led to corrosion of the pipelines, which led to significant leaching of iron and copper in the solution (Lee et al. 2020). Another way is pre-filtration through a nanofiltration membrane (Zhang & Zhang, 2021). Filtration of water through weakly acid cation exchange resin in H^+ form is a very promising method that reduces the formation of scale on the membrane due to acidification of water and removal of hydrocarbons due to degassing of CO_2 (Gomelya et al. 2014). Methods of pre-treatment of water on the cation exchange resin are appropriate for water hardness up to 20 mg-eq/dm^3.

To prevent the formation of a precipitate of insoluble inorganic compounds on the surface of the membranes in the process of reverse osmosis desalination, it is recommended to use antiscalants (He et al. 2009, Yu et al. 2021). Antiscalants should be used for water with a high content of non-carbonate hardness. Necessary doses of antiscalants, which depend on the chemical composition of water, should be calculated according to the programs of reagent suppliers. When choosing an antiscalant, preference should be given to reagents whose molecules contain several functional groups, preventing the formation of precipitates of several chemical compounds. In addition, during operation, compliance with hygienic standards for the content of antiscalants in drinking water should constantly monitored (Armbruster et al. 2019).

The following requirements are set for stabilizers: high efficiency at a low dose, environmental friendliness, and comprehensive action. Therefore, it is important to find new and improve existing reagents that will fully meet the requirements (Yu et al. 2020, Ang et al. 2016). The choice of antiscalant depends on the composition of the water supplied to the RO treatment. In the work (Yin et al. 2021) it is shown that show that amino-enriched antiscalants possess the best performance to mitigate silica scaling created by polymerization, antiscalants with Ca(II)-complexing moieties are the most effective to inhibit gypsum scaling formed via crystallization.

Phosphonic acids are very expensive reagents. The main disadvantage of polyphosphates is the formation of inactive o-phosphates at elevated temperatures during the hydrolysis, which also stimulates biofouling (Huang et al. 2021). In addition, these reagents do not always provide the required degree of stabilization of water treatment. In the work (Liu C. et al. 2021; Liu et al. 2022) it is shown that application of PBTCA in MD system may partly promote biofouling development, DTPMPA posed a risk of MD wetting and secondary fouling of phosphate crystals.

Polymeric antiscalants, in contrast to phosphorus-containing inhibitors, are more resistant to high operating temperatures (Hasson et al. 2011). Therefore, they are not subject to biodegradation, which can have a significant impact on the environment after disposal (Hasson et al. 2011; Matin et al. 2019). Consequently, it is important to develop and examine a highly effective, inexpensive and stable reagent to prevent scale formation.

MATERIALS AND METHODS

A low-mineralized solution, similar in composition to water from Toretsk city: (solution 1), concentrate of RO desalination of water on a low-pressure membrane Filmtec TW30-1812-50, formed at a degree of selection of permeate 80% (solution 2) and 90% (solution 3) were used as a medium. Studies to evaluate the effectiveness of scale stabilizers were performed under static conditions, the volume of solution samples (0.5 dm^3) was kept constant throughout the experiment. The temperature of the solution was maintained at 60°C for 6 hours using a thermostat. Hydrolyzed polyacrylonitrile (gipan) and this reagent were used as inhibitors after sonication for various times. The dose of gipan was 0.5–20.0 mg/dm^3. After cooling, the samples were filtered and the residual water hardness was determined. Stabilizing and anti-scale effects were calculated (Trus et al. 2022).

Table 1. Characteristics of solutions

Parameter	Solution 1	Solution 2	Solution 3
Hardness, mg-eq/dm^3	10.3	51.4	102.9
C(Ca^{2+}), mg-eq/dm^3	3.4	16.9	33.9
C(Mg^{2+}), mg-eq/dm^3	6.9	34.5	69.0
C(SO_4^{2-}), mg-eq/dm^3	15.0	74.8	149.8
C(Cl^-), mg-eq/dm^3	3.1	15.4	30.8

RESULTS AND DISCUSSION

In many industrial regions, fresh water is scarce, but there is a large amount of mine water, which contains high concentrations of salts of calcium, magnesium, carbonates, sulfates and chlorides, resulting in high levels of mineralization. When desalinating these waters, insoluble salts are deposited on the surface of the RO equipment. To increase the efficiency of RO desalination methods of pre-treatment of water or scale stabilizers are used. However, preliminary water treatment requires the introduction of additional equipment, which is technologically and economically impractical. Therefore, the development of scaling reagents for waters of different mineralization degree is more promising. This will ensure high efficiency of water desalination at low cost.

The aim of the work is to develop a highly effective reagent for stabilizing water treatment in the processes of reverse osmosis desalination, which will create closed water consumption systems to ensure the rational use of water resources. To achieve this goal the following tasks are set:

- determination of the effectiveness of gipan as a stabilizer of scale formation for waters of different chemical composition;
- determination the effect of ultrasonic treatment on improving the efficiency of this reagent.

Increasing the temperature of the solution increases the probability of scale formation, while increasing the flow rate, especially in the high range, does not significantly affect the formation of scale (Soukane et al. 2021). Therefore, the initial temperature of the solution was 60°C. As a reagent to prevent the formation of deposits of insoluble salts on the surface of the RO membrane, it is proposed to use gipan. The results on the use of this stabilizer of scale formation are shown in Figure 1. The inhibitor was used at concentrations of 0.5–20 mg/dm^3 when heated to 60°C for 6 hours in a solution with a hardness of 10.2 mg-eq/dm^3. High stability of water against sediments was provided by gipan after ultrasonic treatment.

At an inhibitor dose of 0.5 mg/dm^3, the stabilization effect without and after ultrasound treatment reached 18.4 and 19.7%, respectively. The anti-scale effect (ASE) was 69.9 and 70.4%, respectively. When the dose of the inhibitor was increased to 20 mg/dm^3, this number reached 86.8 and 89.4%, respectively. The anti-scale effect was 95.1 and 96.1% (Fig. 3).

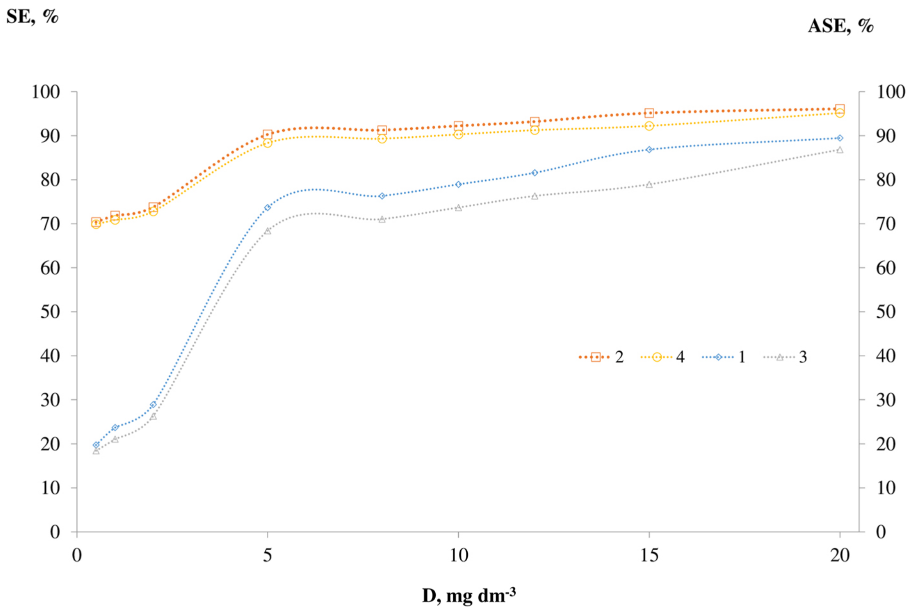

Figure 3. The effect of a dose of gipan at 60°C on water stability (H = 10.2 mg-eq/dm^3) 1, 2 – gipan after ultrasound 20 min; 3, 4 – gipan without ultrasound 20 min; 1, 3 – SE; 2, 4 – ASE

Then the evaluation of the effectiveness of the use of gipan as a stabilizer of scale formation for highly mineralized waters was carried out. As it can be seen from Figure 4, at an inhibitor concentration of 5.0 mg/dm^3, the stabilizing effect (SE) was 29.1%, sonication of the reagent for 5, 10, 20 and 30 min allowed to increase this number to 30.0, 32.0, 37.5 and 38.0%, respectively. Therefore, it is advisable to treat the ultrasound reagent for 20 minutes, as further treatment does not lead to a significant increase in efficiency. At an inhibitor concentration of 20 mg/dm^3, the stabilizing effect reached 42.9% and 82.5% for gipan treated with ultrasound for 20 minutes.

With increasing inhibitor consumption from 0.5 to 20.0, the stabilizing effect increased to from 12.5 to 82.5. At the same time, high values of the anti-scale effect (from 79.0 to 95.8%) were

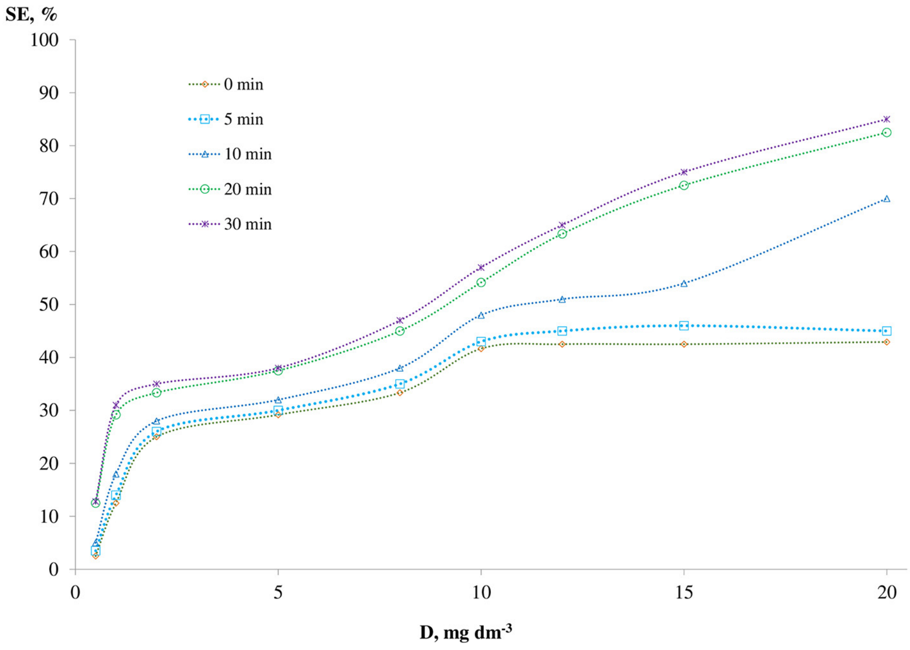

Figure 4. The effect of a dose of gipan at 60°C on water stability at H = 50.0 mg-eq/dm^3 (different processing time ultrasound)

recorded, which is usually greater than SE (Fig. 5). As highly mineralized waters with high hardness are often used in water-deficient industrial regions, stabilization of these waters to sediments is a difficult problem. Therefore, the evaluation of the effectiveness of the proposed sludge inhibitor was carried out by changing the hardness of the mine water concentrate and its heating to a temperature of 60°C in the presence of gipan. As it can be seen from Figure 6, the effectiveness of water stabilization depends on the cost of the inhibitor and the time of treatment of ultrasound. Despite the fact that the water hardness reached 95.0 mg-eq/dm^3, at a dose of gipan 5.0 mg/dm^3 stabilization effect reached 33.3%, when increasing the dose of inhibitor to 20 mg/dm^3 there is an

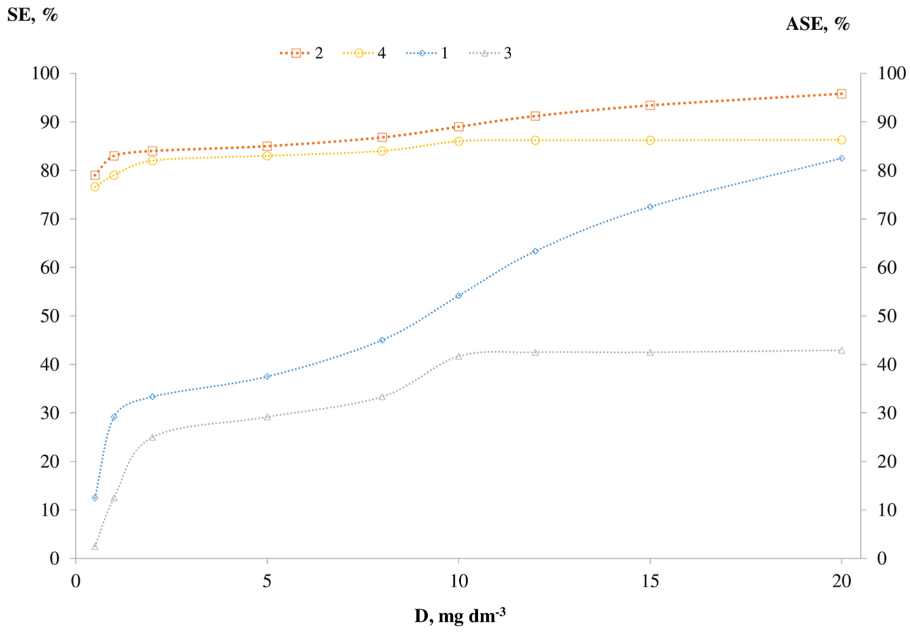

Figure 5. The effect of a dose of gipan at 60°C on water stability (H = 50.0 mg-eq/dm^3); 1, 2 – gipan after ultrasound 20 min, 3, 4 – gipan without ultrasound 20 min; 1, 3 – SE; 2, 4 – ASE

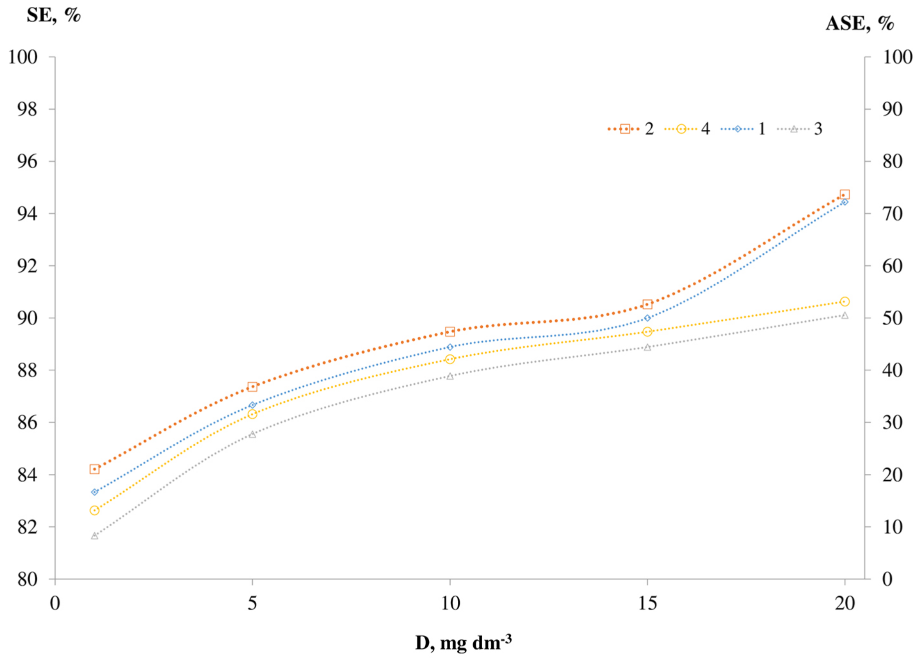

Figure 6. The effect of a dose of gipan at 60°C on water stability (H = 95.0 mg-eq/dm^3); 1, 2 – gipan after ultrasound 20 min, 3, 4 – gipan without ultrasound 20 min; 1, 3 – SE; 2, 4 – ASE

increase in the stabilizing effect to 72.2%. Thus, the development of an effective reagent for stabilizing water treatment can solve the problem of resource conservation, rational use of water and protection of natural reservoirs from man-made impact. Thus, the technological scheme of reverse osmosis desalination of water includes: pre-acidification on the cation exchange resin in H^+ form, the introduction of gipan, which is an inhibitor of scale formation, reverse osmosis desalination, degassing and disinfection.

CONCLUSIONS

An evaluation of the effectiveness of the use of gipan as a stabilizer of scale formation for waters of different mineralization, including highly mineralized waters was performed. This reagent at a concentration of 15–20 mg/dm^3 provides a stabilizing effect at 44.4–50.0%, and the anti-scale effect of 89.4–90.3%. When treating gipan with UV for 20 min, the stabilizing and anti-scale effects reach 50.0–72.2% and 90.5–94.7%.

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