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Suitability of cationic flocculants for RO membranes performance improvement

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ABSTRACT

As it has already been published and demonstrated, one of the main causes of membranes failures is related to a poor plant pretreatment. Data from more than 600 autopsies demonstrated that both biofilm and colloidal matter are the most common components on reverse osmosis (RO) membrane fouling; therefore, main lack on membrane pretreatment is related to disinfection and small size of the particles. The main deficiency in membrane pretreatment is related to the dosing of chemicals such as biocides, and flocculants, which are the only tool for membrane pretreatment improvement. Although on previous papers, cationic flocculants effectiveness was already proved, there is still a reluctance to use these kinds of products on RO pretreatments. Genesys Membrane Products laboratories has broad experience on the optimization of cationic flocculants use which proves the effectiveness of these products for RO pretreatment with no risk for the membranes. This paper will demonstrate the compatibility of some cationic flocculant with membranes, as well as the compatibility of novel formulations including biocides in the flocculant formulation. On this paper, the authors will review data from laboratory tests, case studies, and compatibility tests carried out through different analytical techniques (SEM-EDX, ATR/FTIR, etc.) for the different flocculants developed by Genesys International Limited and will try to demonstrate the safe use of these products for the best performance of RO systems.

Keywords: Cationic flocculants; RO membranes; Compatibility

1. Introduction

Water treatment throughout reverse osmosis (RO) membranes technology is already widely applied, but there is still much effort being done trying to develop membranes with different chemistry and morphology. This effort is still needed in order to improve membrane performance, mainly trying to minimize fouling on membrane surface, since as a matter of fact, fouling is one of the main causes of membrane performance failures [1].

Previous papers demonstrated that, besides biofilm, colloidal matter is one of the main types of fouling detected on membranes surface both as main and secondary components. Although colloidal matter will

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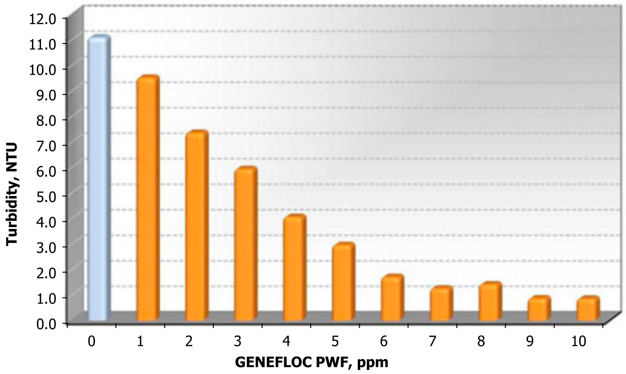


Fig. 1. Turbidity values obtained after Genefloc PWF dosing and later filtration.

gradually affect all membranes, first effects are commonly detected on lead elements [1]. The main consequence of membrane fouling by clay minerals is an increase in hydraulic resistance, resulting in a greater energy requirement to operate process [2]. Besides, in presence of colloidal matter, an increase in Δp is expected and an irreversible damage of the membrane surface may certainly occur as a final consequence.

Due to the common presence of colloidal matter on membranes surface, some specific cleaners have been developed with very successful results [2], but it is necessary to optimize plant pretreatment as much as possible in order to minimize the amount of colloids reaching the membrane anyway.

Even technical membrane manufacturers manuals point out that the best way to remove colloidal matter from water is to agglomerate fine particle size colloids as large particles that can be removed more easily using either media or cartridge filtration [3]. Among the range of pretreatment chemicals that can be used for particles agglomeration, cationic flocculants are particularly effective for colloidal matter removal, but their use in membrane applications is sometimes limited because it is still thought that the use of them can be detrimental to membrane operation [4]. On previous works, we already explained that cationic flocculants can be acrylamide copolymers with a cationic monomer, cationically modified acrylamide or a polyamine. In these polymers, the charge can be located either on a pendant group or in the backbone of the polymer chain [4].

Genesys International manufactures a range of cationic products that have been successfully tested in our laboratory for colloidal particle removal at different water sources. These products improve the performance of the filtration equipment and have been developed as a general purpose flocculant to use in surface, well, and process water with medium to high silt density index (SDI) values. These flocculants are liquid and fully miscible with water, which makes it very easy to handle and dose them. Their names and main characteristics are included below.

Genefloc GPF	Genefloc PWF	Genefloc ABF
Approval for drinking water applications in some countries (local regulations)	This flocculant conforms to European Standard EN 1408:1988 for use in the treatment of water intended for human consumption	Genefloc ABF acts as a combined biocide and flocculant, reducing the effect of colloids, bacteria, and algae on membrane systems
Between 1 and 4 mg/L	Between 2 and 5 mg/L	Between 2 and 10 mg/L

These flocculants should be steadily dosed to the feed water, allowing at least 5 min contact time before filtration. These flocculants are liquid, can be diluted, and are fully miscible with water in all proportions

2. Materials and methods

Jar tests were developed using both turbidity measurements (HACH 2100P ISO) and particle size distribution (Spectrex PC 2200). The use of these different techniques for testing water pretreatment improvement is widely explained on previous papers [5].

Membrane tests were carried out using Hydranautics CPA3 and SWC5 + blanks on a flat test rig using standard solutions of NaCl 1,500 ppm (brackish water) and 32,000 ppm (sea water) and were operated at 225 and 800 psi, respectively.

3. Results and discussion

Genesys Membrane Products laboratory is specialized on RO membrane autopsies and, as a complement of these autopsies, the lab carries out analyses of different components from plants pretreatment. Over the last 10 years, GMP laboratory has developed more than 750 membrane autopsies, 300 cartridge filters, and around 350 SDI filters.

SDI filters analyses are the best way to identify the nature of suspended matter in water. Among common components detected on these filters are colloidal matter (aluminosilicates) metals (both as oxide and as particles from corrosion drags), micro-organisms (diatoms, e.g.), and organic matter. Although all these components have been detected on SDI filters in our labs, the most common component identified on most of them is *colloidal matter*.

Another useful tool to identify suspended matter is cartridge filters analysis. The identification of the matter retained on security filters gives valuable

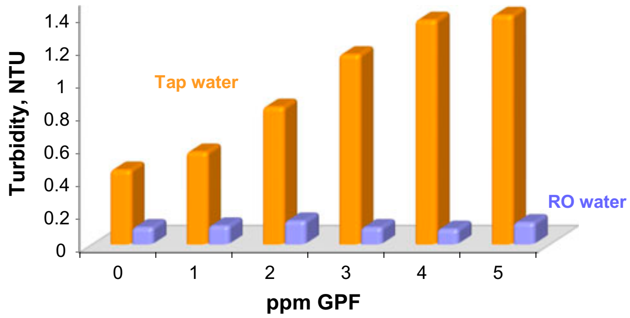


Fig. 2. Turbidity values of a tap water sample after flocculant dosage, compared with a RO water with no particles.

information on the matter which has not been retained on the previous treatment process, most commonly a sand filter. On the other side, the analysis of these filters can also give information about microfilters efficiency. Photographs 1–3 show some examples of cartridge filters with a different fouling on the surface. Besides, some microphotographs from different kind of filters fouling are included. As for SDI filters, aluminosilicates (colloidal matter) are the most common component detected on microfiltration systems.

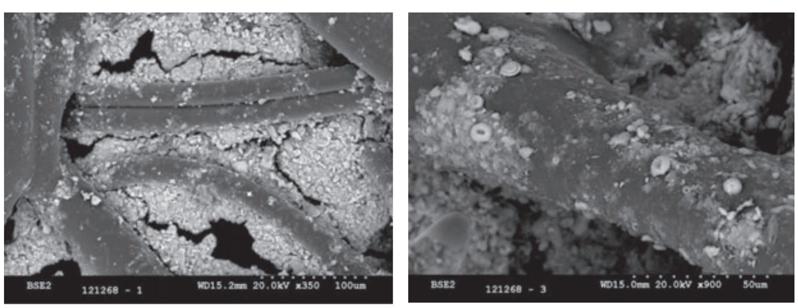
Depending on the amount of matter that may reach these security filters, they will be able to work more or less efficiently and aluminosilicates might pass through and eventually reach membranes surface. When different SDI membranes disks from the different pretreatment components are analyzed, it is quite common to verify that there is a decrease in the presence of the aluminosilicates from the raw water to the RO inlet water. However, in many cases, we have detected that the quality of water concerning suspended matter gets worse after cartridge filtration. This is mainly, because when filters get overloaded, there are leakages from them to the RO system.

On the other side, when both autopsies and cartridge filter analyses from the same plant are carried

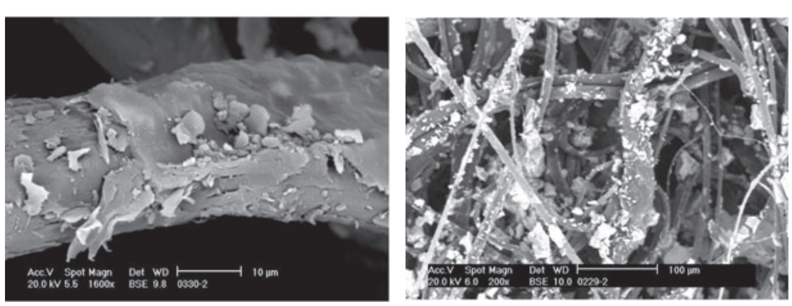
Photograph 1.-Fouling on both external and internal surfaces

Photograph 2.-Fouling on external surface filter

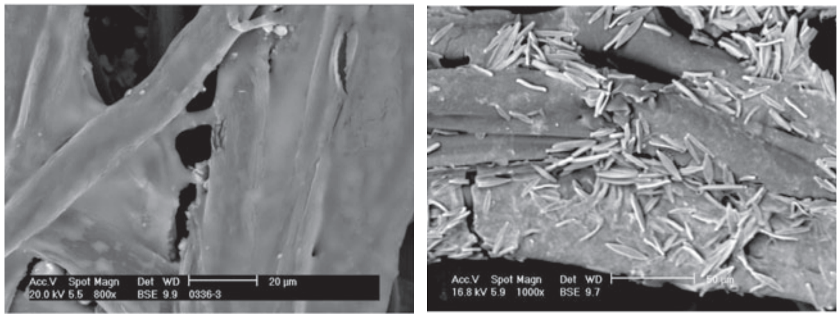
Photograph 3.-Fouling on internal surface filter



Microphotographs 1.- Cartridge filters fouled by aluminosilicates / colloidal matter



Microphotographs 2.- Cartridge filters fouled by organic matter + calcium carbonate (left) and metals (right)



Microphotographs 3.- Cartridge filters fouled by organic matter (left) and diatoms (right)

out, the same fouling is mostly found on both cartridge filter and membrane surface.

As already explained, aluminosilicates are one of the most common components of RO membranes fouling, both as main and secondary. Besides a decrease in the permeate flow, the last consequence of aluminosilicates presence on membrane surface is an increase in delta p. Thus, there is a clear risk of damage of the membrane surface by a possible spacer protrusion, marks from spacer or abrasion marks. The following microphotographs show examples of damage on membranes with a relevant presence of aluminosilicates on the membrane surface. All this data indicate once more the need of colloidal matter removal prior to RO membranes.

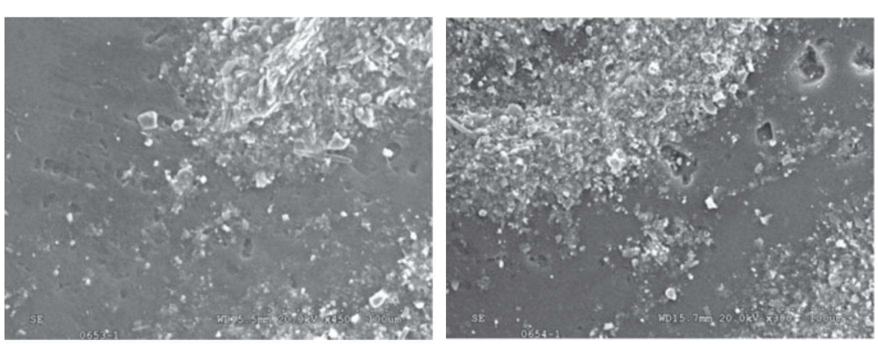
3.1. *Jar test results*

As already mentioned, the best way to remove colloidal matter from water is to make fine particles agglomerate into larger particles using coagulants and/or flocculants and to retain them on a filtration system. The best tool in the selection of the most suitable flocculant for colloidal matter removal is a jar test.

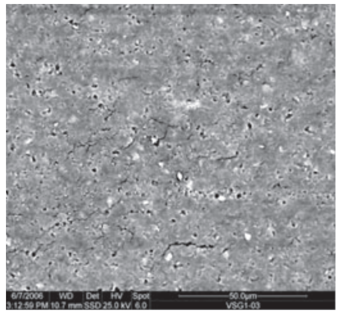
When a jar test is developed for a settling or DAF process, it is necessary to look for a big floc with settling or floating characteristics. But colloidal matter removal must be carried out through a filtration process and this requires to get microflocs with no real settling or floating properties. In many cases, it is not possible to detect these microflocs visually.

On the other side, the main effect of this kind of compounds in water pretreatment is the improvement of SDI values, but this parameter cannot be measured in laboratory. The only test that could relate SDI measurements and laboratory tests would be to verify the efficiency of flocculants on SDI value reduction. The following microphotographs 5 and 6 show SDI filters surface obtained after raw water filtration and after filtration of the water obtained after flocculant dosing. As it can be observed, it is not possible to distinguish filter structure on SDI filter from raw water (Microphotograph 5). With the increase in flocculant dosing, a filter structure could be distinguish and SDI values were lower than before the use of the product (microphotograph 6).

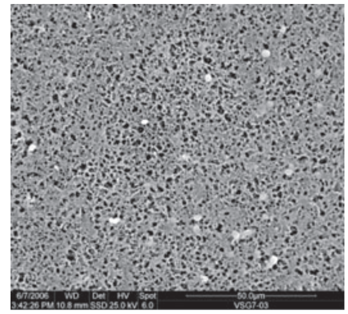
Provided the impossibility of testing SDI values in a laboratory, water parameters related to suspended matter such as turbidity or particle size distribution are the best way to demonstrate if a product is suitable for particle agglomeration [5]. Next chapters will include results obtained during jar tests carried out with the different cationic flocculants manufactured by Genesys International.



Microphotographs 4.- Damage on membranes surface due to the presence of aluminosilicates



Microphotograph 5.- SDI filter obtained after raw water filtration. SDI value: no measurable (infinite)



Microphotograph6.- SDI filter obtained after 5 ppm flocculant dossing. SDI value: 4.3

3.1.1. Genefloc PWF results

This product conforms to European Standard EN 1408:1988 for use in the treatment of water, intended for human consumption. It has been applied at different sites working with different kinds of water, volume production, and application, combined with different antiscalants. At all these sites, Genefloc PWF has been successfully applied.

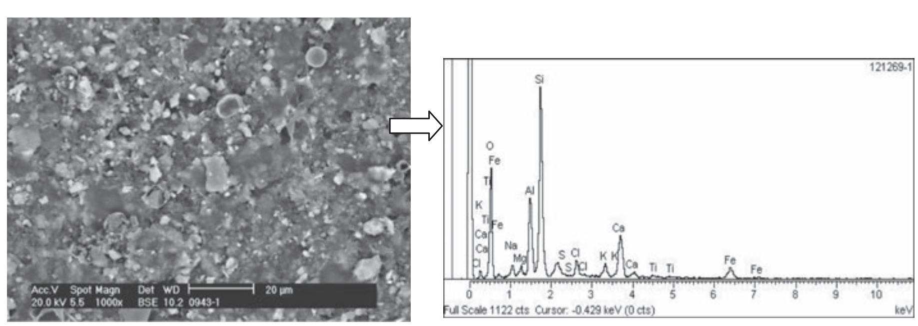
As the rest of flocculants studied for this paper, Genefloc PWF is very successful on colloidal matter removal. As an example, the following microphotograph 7 shows an SDI disk surface completely fouled by aluminosilicates (colloidal matter). This study corresponds to a well water with a very high turbidity level (19.1 NTU), which even filtered through 20–25 µm, still gave a turbidity value of 11.0 NTU. Fig. 1 included below shows how with an increasing dose of Genefloc PWF, there is a very relevant decrease in filtered water turbidity, reaching values even lower than 1 NTU with 9 ppm of product.

3.1.2. Genefloc GPF results

Genefloc GPF is our most frequently used product. It has been successfully tested on 95% of the jar test carried out in our laboratories. The high number of tests developed using this product has enabled us to verify that, besides fine colloidal particles agglomeration, it can be successfully applied in water samples with suspended matter of very different nature: colloidal silica, metallic particles, etc.

Next, Fig. 2 represents some turbidity values obtained during a jar test with GPF working with a water sample with a low turbidity, but high SDI values. When water has low turbidity, an increase in turbidity values will be related to the formation of microflocs. This increase in turbidity will only be detected on the samples with suspended matter, since no turbidity increase in water without suspended matter (RO water in this Fig. 2). If we look into particles size distribution of this sample during jar test (see Fig. 3), it can be verified how after dosing of the flocculant the maximum percentage of particles detected shifted to a higher particle size.

Besides the agglomerate of fine particles, another advantage in the use of cationic flocculants is that they help to decrease metal residual concentration from the coagulants used during pretreatment of water prior to filtration process. To illustrate this, the following Figs. 4 and 5 include some real iron and aluminum concentration values, which suffered a relevant decrease when a cationic product was used during filtration.



Microphotograph 7.- SEM image of an SDI disk completely covered by aluminosilicates (clay/colloidal matter)

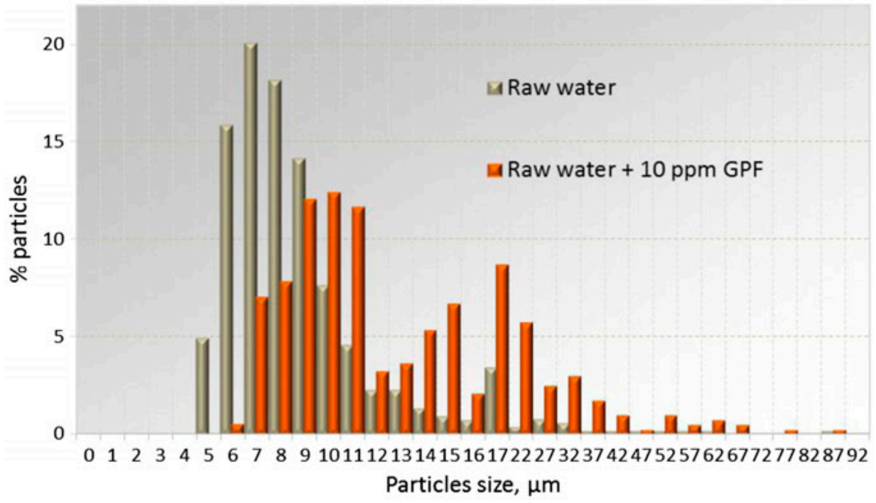


Fig. 3. Particle size distribution of a water sample after additional dosage of flocculant.

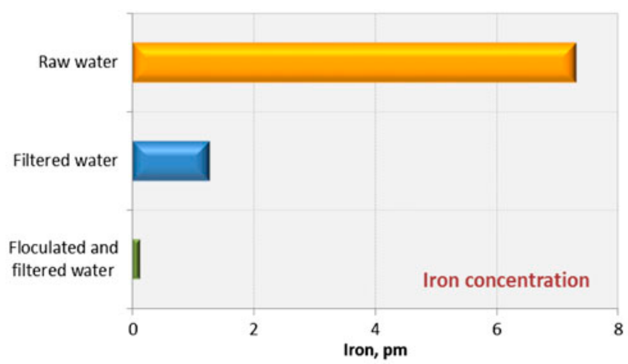


Fig. 4. Iron concentration during filtration process with and without flocculant (Genefloc GPF).

3.1.3. Genefloc ABF results

Genefloc ABF combines different active ingredients in order to provide different properties: flocculant, biocide, and algaecide. Genefloc ABF reduces water surface tension and acts on the normal functions of cell membranes preventing growth. Genefloc ABF interacts with the phospholipids of the cell membranes of micro-organisms while another nonpolar molecule of this product enters the cell decreasing cell membrane permeability and changing its protein activity. Although its optimum activity is at pH values higher than 7, it can be used at any pH range.

Due to this fact, and depending on the kind of water, this product may be more suitable as a flocculant or as a biocide.

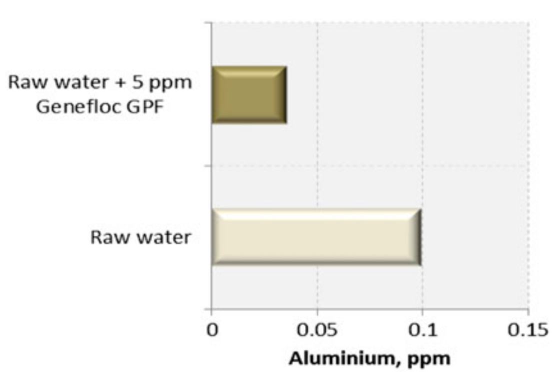


Fig. 5. Aluminum concentration during filtration process with and without flocculant (Genefloc GPF).

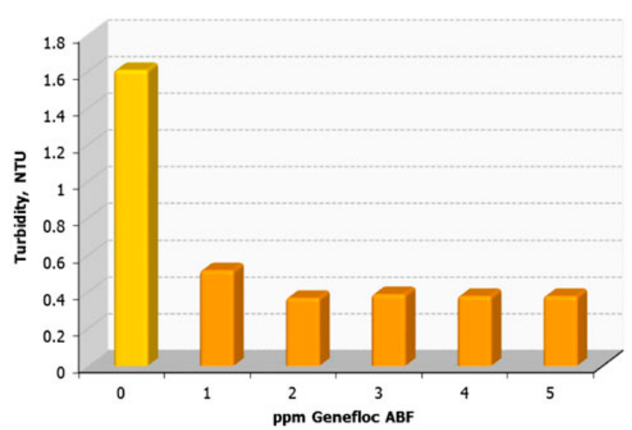


Fig. 6. Filtered water sample turbidity after different Genefloc ABFs dosing.

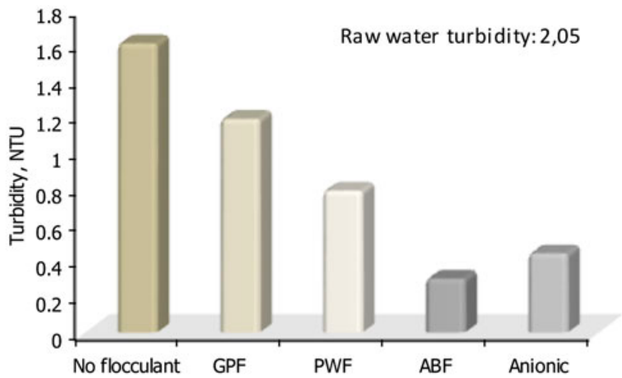


Fig. 7. Filtered water samples turbidity after different flocculants dosing.

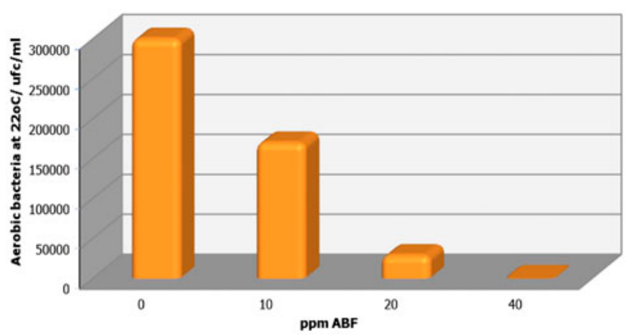


Fig. 8. Genefloc ABF activity against aerobic bacteria.

When acting as a flocculant, many tests carried out in our laboratories demonstrate that Genefloc ABF is a suitable product for agglomeration of fine particles. Fig. 6 shows filtered water samples turbidity after an increasing ABF dose. As this figure shows, filtered water turbidity suffers a relevant decrease from the first tested concentration.

On the other side, the characteristics of this product depict that some waters can provide a similar performance to anionic flocculants (mainly against organic suspended components). As an example, Fig. 7 includes a comparison of the turbidity obtained from different flocculants addition to a surface water sample. As it can be observed in this water sample, although GPF and PWF achieve a successful decrease in turbidity, Genefloc ABF allows the lowest turbidity value. The result obtained with this flocculant is even better than the one obtained when using an anionic flocculant, which is supposed to work better with surface water.

As explained before, Genefloc ABF shows biocide characteristics that make it active against some microorganisms. The following Fig. 8 illustrates a relevant reduction of aerobic bacteria when ABF dose is increased. Therefore, this product is broadly applied as biocide on systems which cannot control chlorine or mainly when there is a high presence of algae, although there are also many applications of it as flocculant.

3.2. Flocculants compatibility tests

Genesys cationic flocculants have been successfully applied in field and no relevant changes on membranes performance have ever been detected. On the other side, from the 750 autopsies developed in our laboratories, only on 1% of them fouling was related to flocculants. These flocculants were polyacrylamide derivatives, not cationic flocculants.

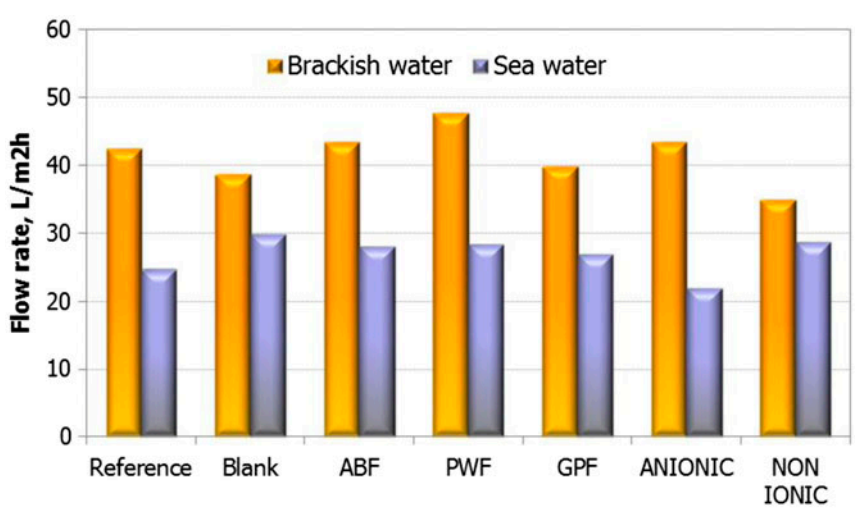


Fig. 9. Permeate flow rate performance parameters after soaking period in 1 g/L flocculant solution.

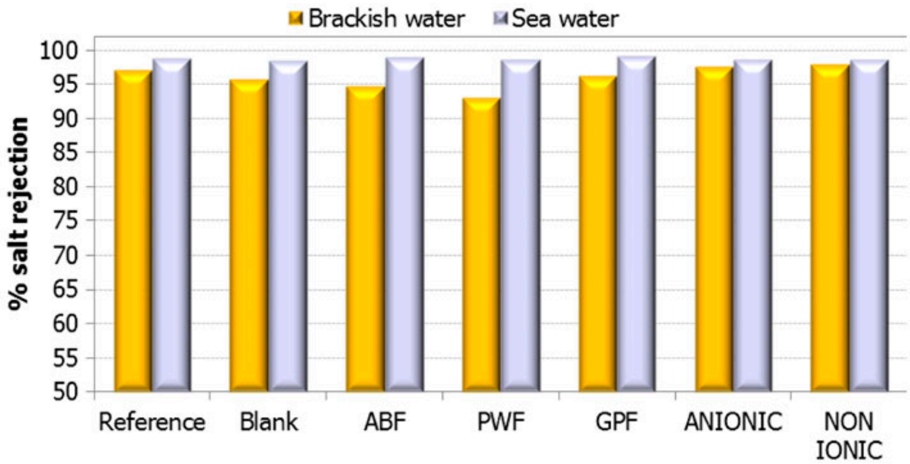


Fig. 10. Salt rejection percentage performance after soaking period in 1 g/L flocculant solution.

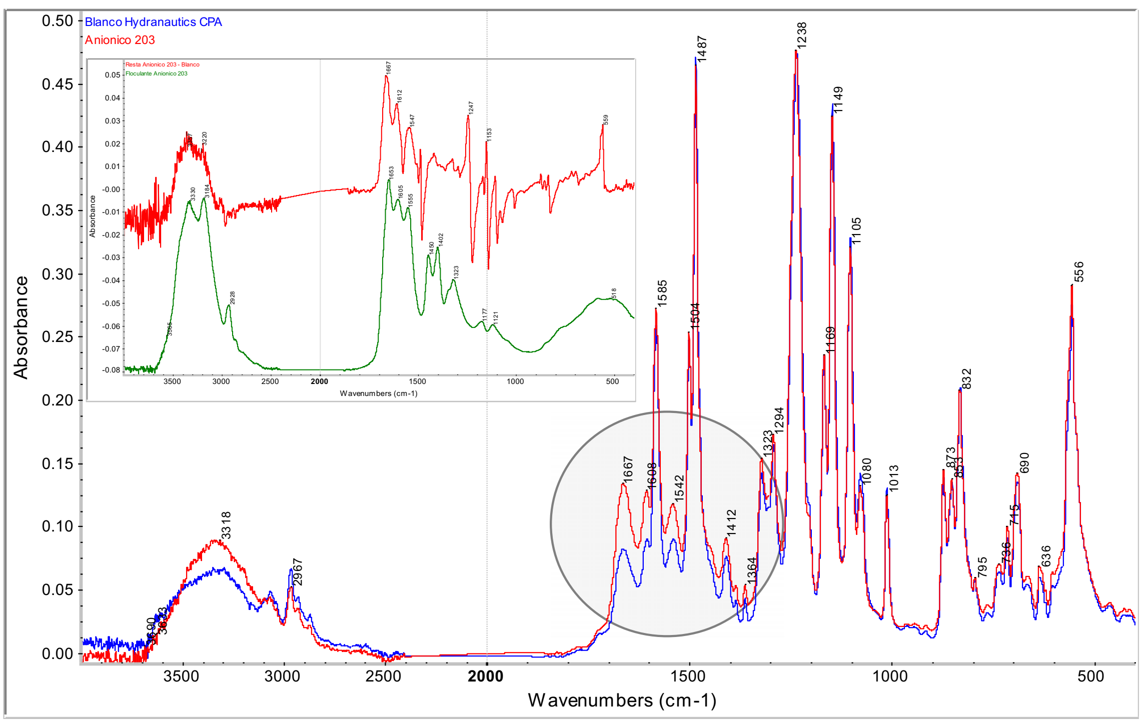


Fig. 11. Comparison of anionic coupon after soaking period to blank membrane spectra (brackish water).

Anyhow, some tests were developed in Genesys Membrane Products laboratory in order to understand as much as possible about the compatibility of flocculants and membranes. These tests were carried out checking the performance of membrane after being in contact with an overdosing of flocculants through two different ways:

- Soaking tests: membrane coupons were soaked during one week in a 1 g/L flocculant solution and after that period, both membrane performance parameters and membrane surface were analyzed.
- Compatibility tests during membrane performance: these tests were carried out by adding

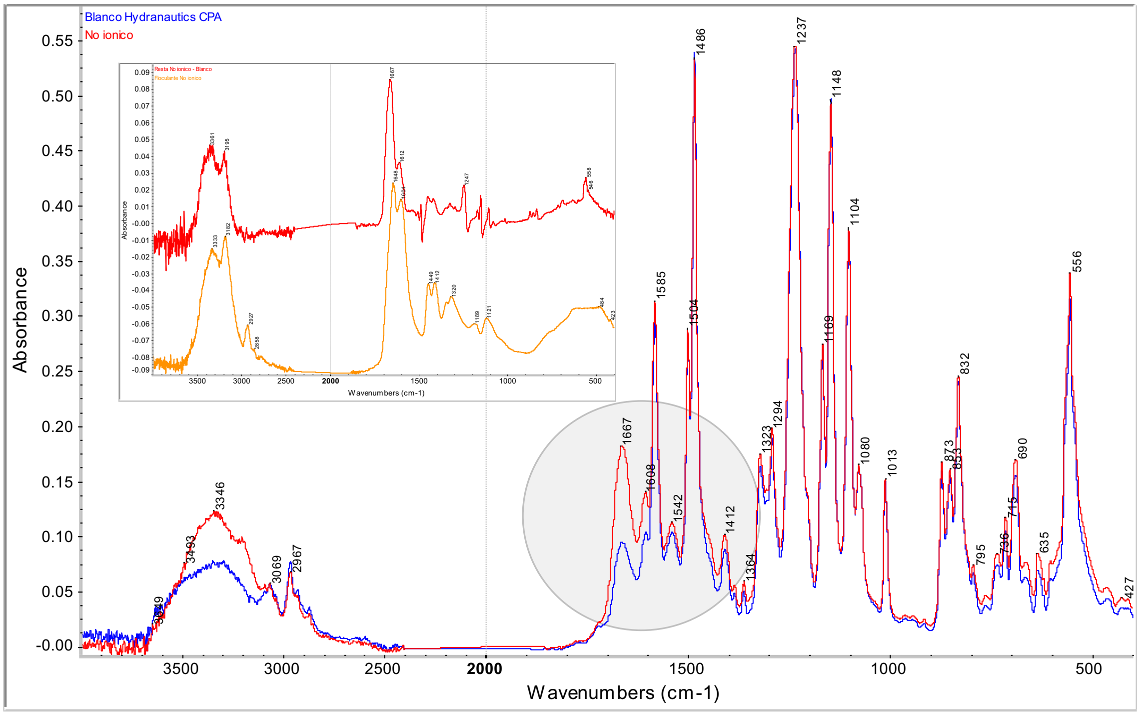


Fig. 12. Comparison of nonionic coupon after soaking period to blank membrane spectra (brackish water).

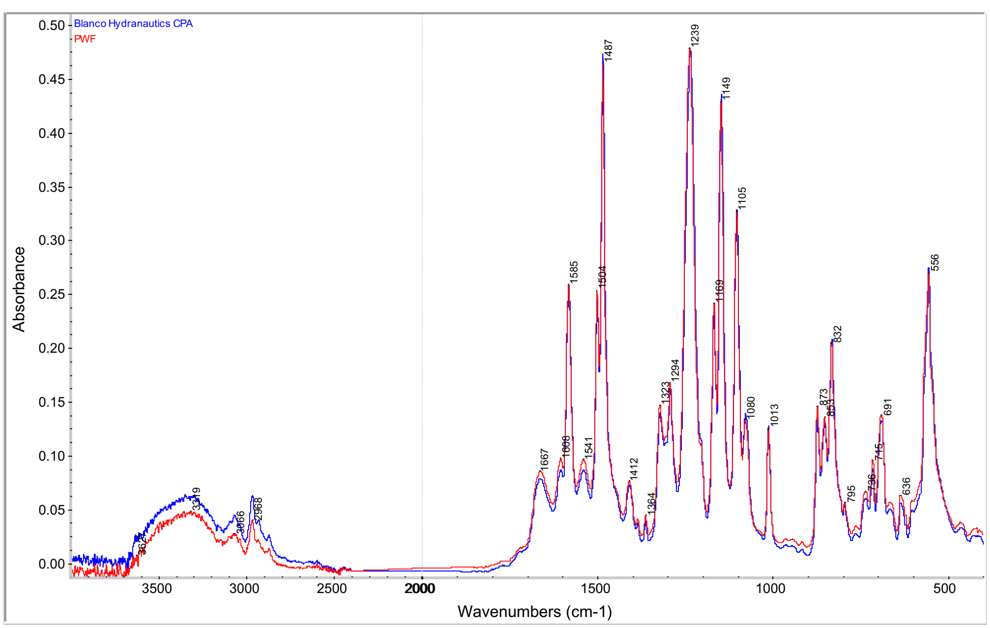


Fig. 13. Comparison of PWF coupon after soaking period to PWF flocculant spectra (brackish water).

100 ppm of flocculant during membrane operation and performance parameters were measured during 4 h.

3.2.1. Soaking tests

Figs. 9 and 10 represent flow rate and salt rejection percentage values after a period of one week soaking

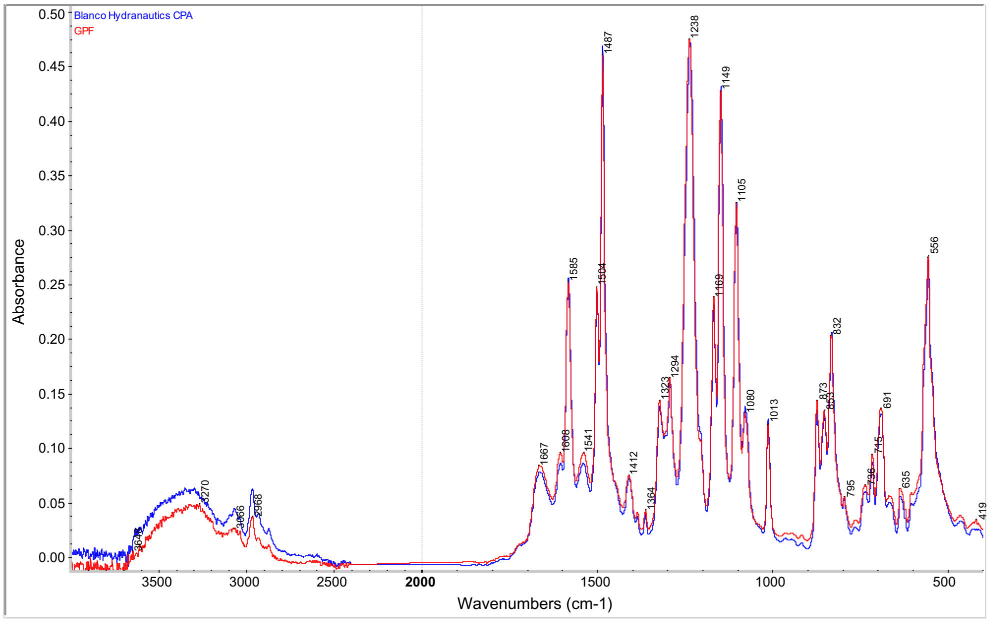


Fig. 14. Comparison of GPF coupon after soaking period to blank membrane spectra (brackish water).

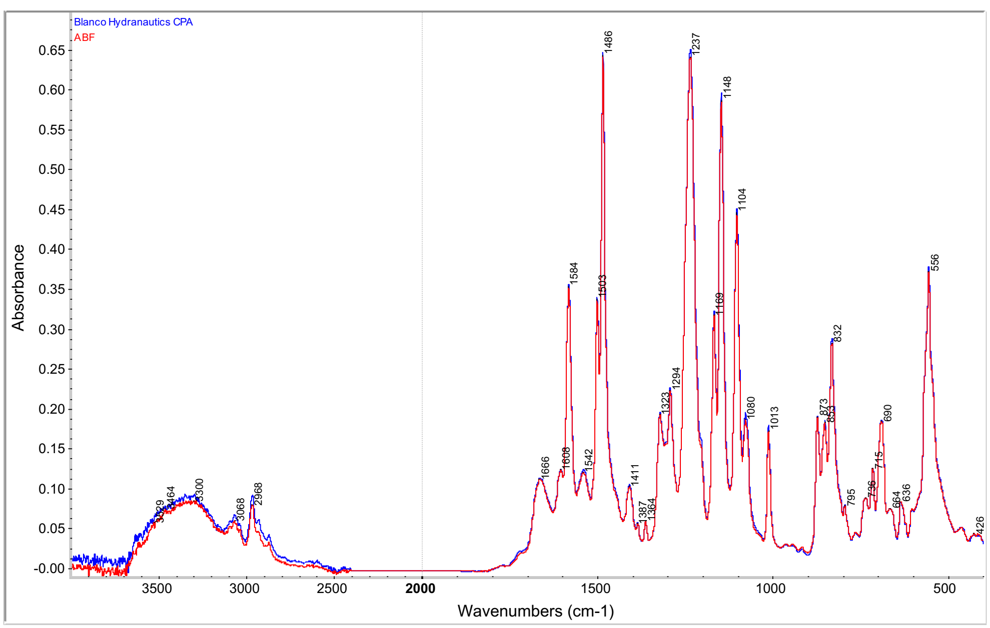


Fig. 15. Comparison of ABF coupon after soaking period to blank membrane spectra (brackish water).

in 1 g/L of each product. As it can be observed, the soaking period does not affect the performance of membrane coupons with none of the cationic flocculants tested.

A lower permeate flow rate was observed after soaking period in anionic flocculant for sea water membrane and in nonionic flocculant for brackish water membrane.

As complement to these parameters, both SEM-EDX and ATR-FTIR analyses were carried out on the coupons obtained after flocculants soaking period.

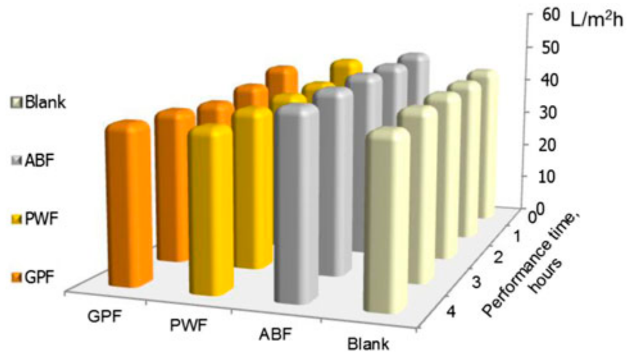


Fig. 16. Brackish water membrane performance after flocculant dosing.

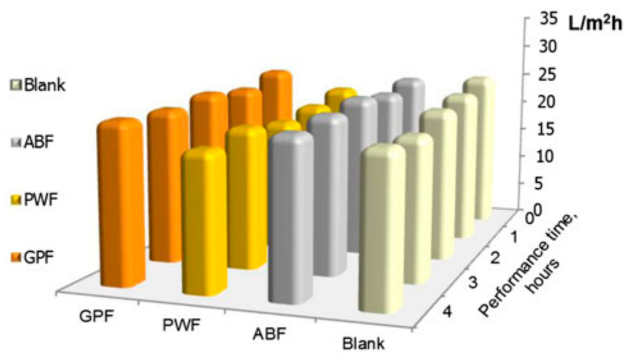


Fig. 17. Sea water membrane performance after flocculant dosing.

No presence of flocculants was observed on none of the sea water membrane coupons after the soaking period.

Concerning brackish water membranes, SEM-EDX analyses revealed presence of an organic component on the anionic flocculant coupon (see Microphotograph 3). Besides, IR analyses showed that only membrane coupons obtained after contact to anionic (Fig. 11) and nonionic flocculants (Fig. 12) showed some IR bands different that those from membrane composition and showed coincidences to flocculants presence. There is no way to demonstrate by this technique whether the presence of these flocculants is due to a reaction or just a deposition.

However, what these results demonstrate is that none of the cationic flocculants show a reaction or direct effect on polyamide layer (Figs. 13–15).

In addition to these tests, further studies were performed to determine possible changes on the performance of membranes after flocculant overdosing. In this case, flow rate was checked during a period of 4 h after dosing 100 ppm of each flocculant, except for Genefloc ABF which was tested at 500 ppm (dose used for disinfection). Fig. 16 corresponds to a comparison of the flow rate obtained from a brackish membrane blank compared with the performance obtained from same membrane model after adding 100 or 500 ppm of each flocculant.

As it can be observed, membrane blank coupon already shows a small decrease in flow rate as time goes by. With the dosing of flocculants, this decrease in flow rate is slightly higher, although none of them

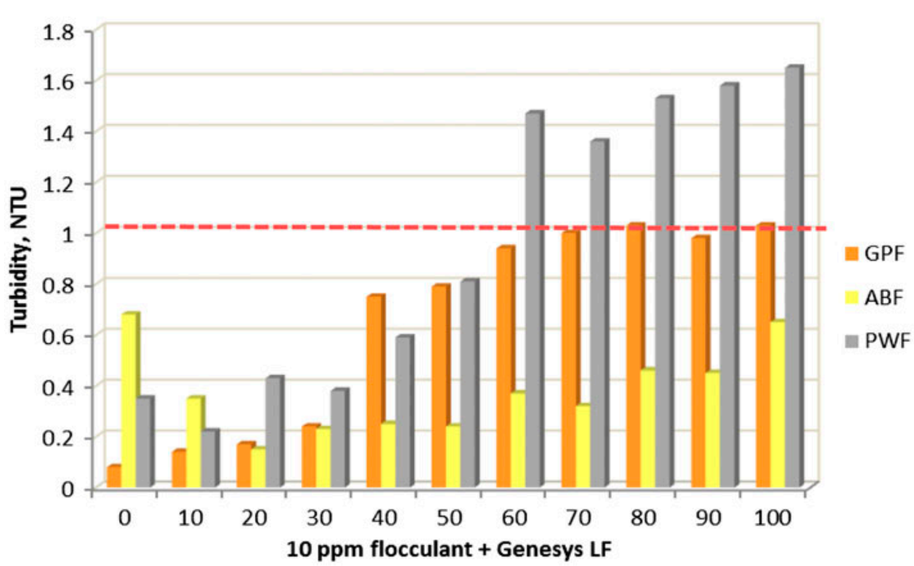
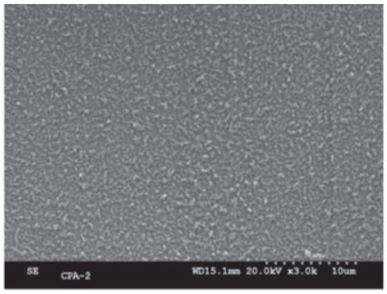
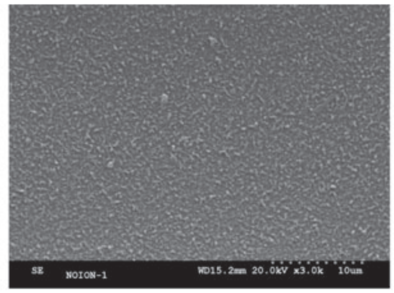


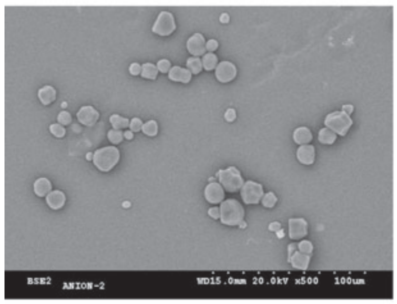
Fig. 18. Turbidity changes after Genesys LF dosing on a 10 ppm of flocculant solution—demin water.



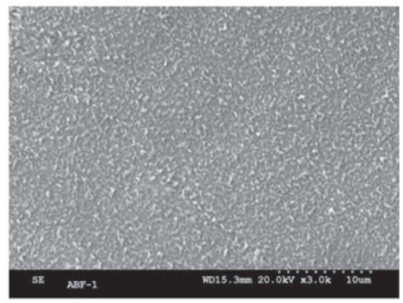
Microphotograph 1.- Detail of membrane blank surface (brackish water)



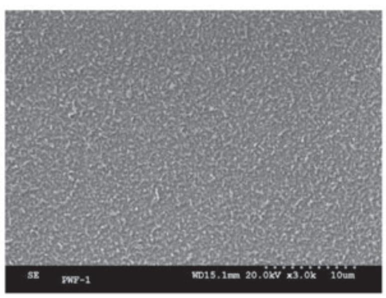
Microphotograph 2.- Detail of membrane surface after soaking on non ionic flocculant solution (brackish water)



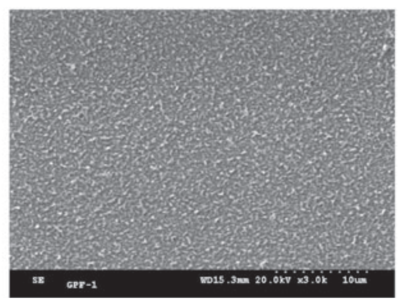
Microphotograph 3.- Detail of membrane surface after soaking on anionic flocculant solution (brackish water)



Microphotograph 4.- Detail of membrane surface after soaking on ABF flocculant solution (brackish water)



Microphotograph 5.- Detail of membrane surface after soaking on PWF flocculant solution (brackish water)



Microphotograph 6.- Detail of membrane surface after soaking on GPF flocculant solution (brackish water)

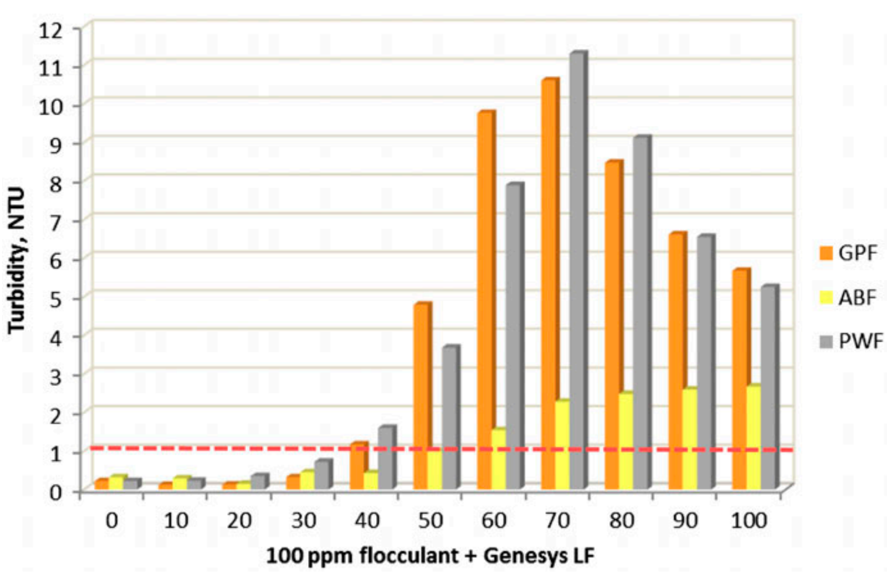


Fig. 19. Turbidity changes after Genesys LF dosing on a 100 ppm of flocculant solution—demin water.

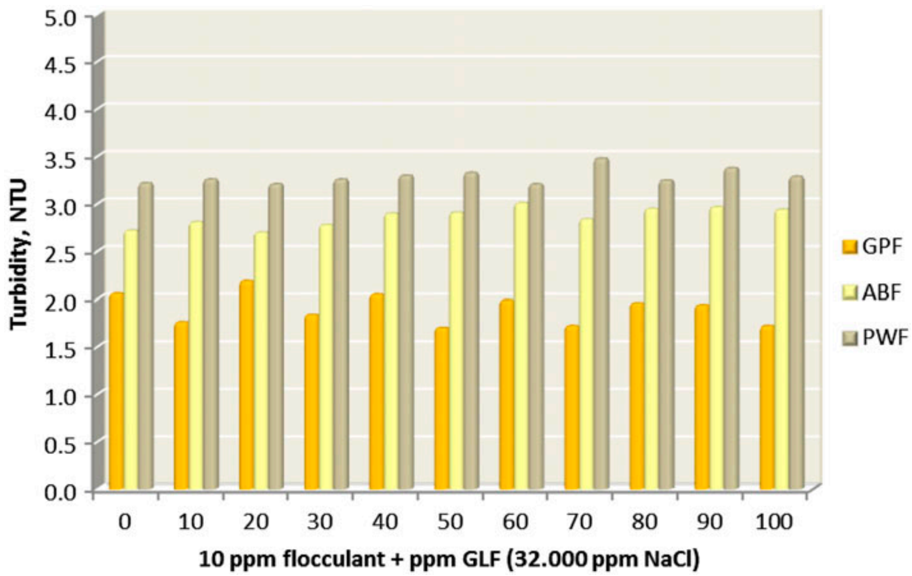


Fig. 20. Turbidity changes after Genesys LF dosing on a 10 ppm of flocculant solution—sea water.

showed a change higher than a 15% (common coefficient of variation admitted by membrane manufacturers for individual elements). In any case, trying to prevent an eventual fouling after overdosing these products, a 2 h cleaning procedure with an alkaline product (Genesol 703) was carried out on these coupons and the flow rate was easily recovered on all of them.

These results indicate that although a slight fouling could happen on membrane surface after overdosing the cationic flocculants tested, this would not be due to any reaction between polyamide and flocculant, and that membrane performance could be recovered after a conventional cleaning. However, since membrane blank also suffers a decrease during performance, it is very difficult to determinate whether this different behavior could be attributed to the flocculant.

The changes observed during this test with brackish water membranes were even lower for sea water membranes (Fig. 17).

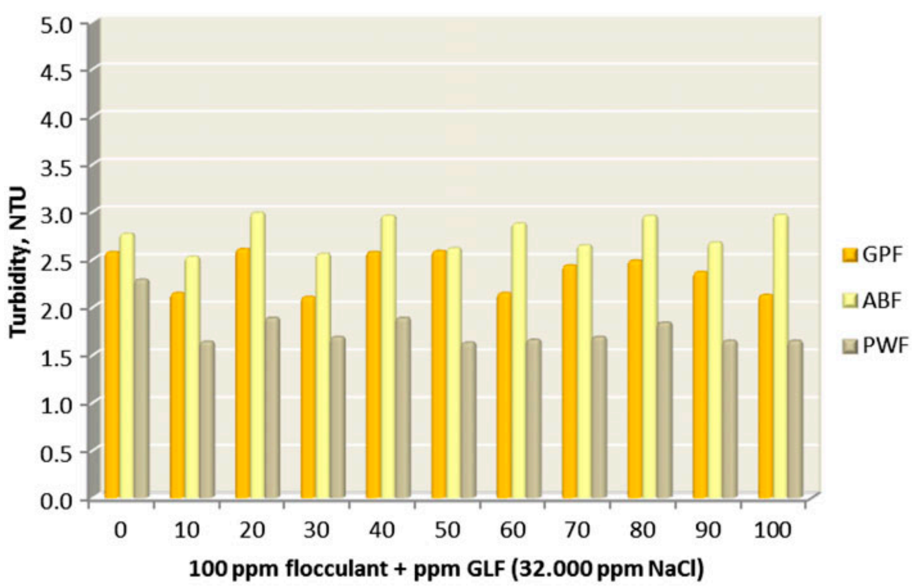


Fig. 21. Turbidity changes after Genesys LF dosing on a 100 ppm of flocculant solution—sea water.

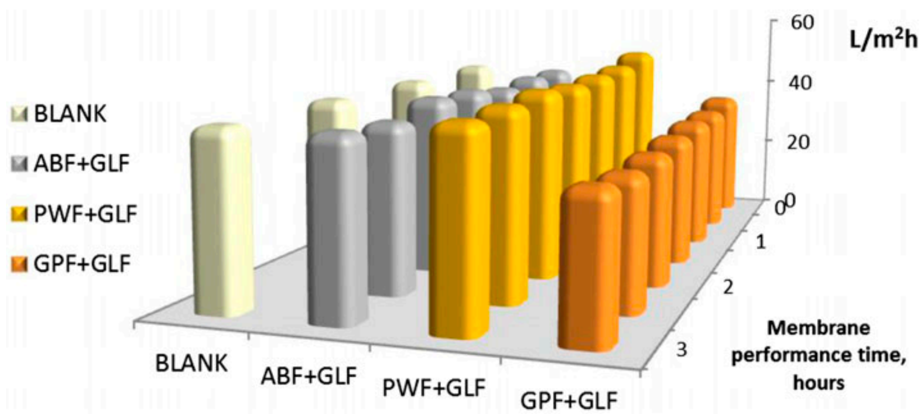


Fig. 22. Permeate flow rate membrane performance after 100 ppm GLF and 100 ppm flocculants dose.

3.3. *Flocculants interaction to antiscalant*

Besides a possible interaction between membrane polyamide layer and cationic flocculants, there is also a belief that cationic flocculants will react to antiscalant due to its negative charge, forming a dangerous gel for membrane performance. In order to know as much as possible about this interaction, some tests were carried out in our labs with Genesys cationic flocculants and the most widely used antiscalant manufactured by Genesys: Genesys LF.

For this test, different doses of Genesys LF were added to 10 ppm (see Figs. 18 and 20) and 100 ppm of each flocculant (unrealistic overdosing, see Figs. 19 and 21). These tests were based on turbidity measurements, considering that an increase in turbidity values will be related to an interaction between flocculant and antiscalant. These tests were carried out both on a demin water and on a 32 g/L of NaCl solution.

As it can be observed in Figs. 18 and 19 (demin water), turbidity remains mainly stable on both 10 and 100 ppm of GPF and PWF flocculant, until a dosing of **40 ppm of Genesys LF.** This effect is not so relevant for flocculant ABF and the increase in turbidity is not so significant at a very high concentration.

Concerning the behavior of antiscalant vs. flocculant at sea water systems, the following graphs show the same study in high salinity water. According to these graphs, sea water does not show any relevant change after antiscalant addition to a fixed flocculant concentration.

Even though a very high overdosing of both flocculant and antiscalant is necessary for an interaction between them, additional tests were carried out in order to know the effect of this mixture on membrane performance. In this case, these tests were only carried out on brackish water membranes, because these are the systems that use a higher concentration of antiscalant.

The following Fig. 22 shows flow rate change during 3 h of membrane performance after a 100 ppm Genesys LF dosing and 100 ppm of each cationic flocculant. As it can be observed, there is not a relevant change on flow rate membrane performance, which indicates that membrane does not suffer a sudden change.

The different tests developed in our labs indicate that despite the cationic nature of Genesys flocculants, there is not a significant change on membrane performance if it gets in contact with a flocculant overdosing of with a flocculant + antiscalant overdosing.

4. Conclusions

- Flocculants studied in this work are very efficient for agglomeration of fine particles, so they can be used to improve filtration processes performance, mainly for colloidal matter removal.
- Both turbidity and particle size distribution analyses are perfect tools for the study of these flocculants in water, since they are the only way to verify the microflocs obtained in most of the samples.
- These flocculants do not show any relevant interaction to membranes surface.
- Overdosing of these products achieve a minimum effect on membranes performance.
- Flocculants and antiscalant GLF only showed some interaction at very high and unrealistic concentration. Contact of this mixture to membrane did not show any relevant change on performance.

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