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Aquatic humic substances, iron, and manganese removal by ultrafiltration and nanofiltration membranes combined with coagulation–flocculation–sedimentation

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ABSTRACT

Iron and manganese removal is made conventionally by oxidation methods; however, when aquatic humic substances (HS) are present, they can affect the removal, with another treatment process being necessary. This study focused on performance of ultrafiltration (UF) and nanofiltration (NF), preceded by coagulation, flocculation, and sedimentation stages for iron, manganese, and HS removal, with two water sources that present superior levels of humic compounds, and measured by dissolved organic carbon (DOC) and UV absorbance at 254 nm. Coagulation, flocculation, and sedimentation combined with UF/NF efficiently removed dissolved iron, HS, apparent color, and turbidity. Almost total iron removal was already attained in the prior steps of coagulation, flocculation, and sedimentation, obtaining final values of dissolved iron of less than 0.001 mg L^{-1} for the two types of water studied. However, the complete system did not appear effective (less than 50% efficiency) in dissolved manganese removal, although a significant reduction in the HS was achieved (approximately 80% after UF and 90% after NF measured as DOC, for two types of water). Pretreatment was shown to be effective in reducing the loss of filtration flow because of the removal of high-molecular-weight HS, thus minimizing the formation of fouling on the membrane.

Keywords: Aquatic humic substances; Iron removal; Manganese removal; Membrane filtration

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1. Introduction

The groundwater and surface water used as sources for human consumption may have substances that are not within the standards for drinking water, either by affecting the organoleptic properties of water or by causing some health problems. Humic substances (HS), iron, and manganese are some of these substances and should be removed from water as part of the water purification process.

In water, iron and manganese can be found in reduced forms under anoxic conditions [1] or can form complexes with humic matter [2,3]. These two elements are oxidized by atmospheric oxygen or by chlorine used for water treatment, producing an esthetic dark precipitate that imparts taste to water, stains clothes and utensils, and forms deposits on the pipes by reducing the transport capacity and causing pressure loss in the distribution system [4,5]. Usually, iron removal is accomplished by oxidation of the ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) by aeration, followed by removal as iron hydroxide ($Fe(OH)_3$) by adjusting of the pH or by direct precipitation of the ferrous ion as hydroxide ($Fe(OH)_2$) through lime (CaO) addition [6,7]. Manganese removal could be achieved by the addition of oxidants (potassium permanganate, chlorine, hypochlorite, chlorine dioxide, or ozone), a method that may result in the formation of toxic compounds [4]. Aeration and precipitation are ineffective due to the use of oxygen that permits a slow oxidation with pH less than 9, which is naturally found in natural waters [8].

Aquatic HS interfere with the esthetic quality of the water, causing color, odor, and unpleasant taste [1]. HS are heterogeneous organic materials that result from the microbiological degradation of vegetable and animal residues, and they can be produced *in situ* or transported by rain by percolating the soil [1,9]. These substances are classified into humin, mostly found in the solid phase; humic acid, with more aromatic character, molecular weights between 2,000 and 5,000 Da, and solubility in pH greater than 2 [10,11]; and fulvic acid, with molecular weights between 500 and 2,000 Da and more aliphatic structures with higher oxygen levels, rich in phenol, carboxylic acid, and ketone groups, which confer solubility at any pH [12] which is why they correspond to 90% of HS dissolved in natural waters [13,14]. HS are associated with physical, chemical, and biological processes (including adsorption, coagulation, acid–base interactions, complexation, oxidation, reduction, hydrolysis, photochemical reactions, transportation, or dispersion of chemicals) [11]. Humic compounds can also form trihalomethanes or other nervous system disruptors, and carcinogenic and mutagenic halogenated substances when water is chlorinated for disinfection [12].

For humic acids, removal methods such as coagulation, flocculation, filtration, oxidation, biological, and adsorption on activated carbon are used; however, these treatments have some problems in their implementation and effectiveness. Biological methods have less than 40% efficiency and require long periods of degradation; oxidative processes have limited capacity and have high operating costs. By coagulation and flocculation, HS removal reaches 60% [15].

Low-pressure membranes (microfiltration and ultrafiltration (UF)) are considered ineffective in removing dissolved organic substances (between 5 and 30% efficiency). The nanofiltration (NF) membranes may reject 50–90% of HS, depending on the molecular weight cutoff membrane [16,17]. The addition of coagulants as pretreatment of membrane filtration increases the efficiency of removal of HS, removing up to 90% by UF spiral aeration systems using $FeCl_3$ as a coagulant and sedimentation [18].

Fe^{2+} and Mn^{2+} without pretreatment are not efficiently removed by the membrane filtration systems, except for reverse osmosis; despite this, they may be retained by UF and NF systems through the formation of complexes with HS present in water [4,19]. The presence of carboxylic and phenolic groups in HS enables their complexation with metallic ions by ionic or covalent bonds, altering their availability, speciation, distribution, and transport properties [2,20].

The strength of binding between HS and metals is determined by the apparent molecular size of HS, the metal species, ionic strength, pH, and complexation time. The force of these interactions can be expressed by the stability constant of the complexes (K_f) [20,21], which refers to the degree of association between the two species at equilibrium [3,22].

This study compares two membrane separation processes, UF and NF, both combined with a coagulation, flocculation, and sedimentation system, to evaluate their efficiencies in removing HS, iron, and manganese from surface and well water.

2. Materials and methods

Lake water and groundwater with high levels of organic matter were chosen for this study. Groundwater possesses higher concentrations of dissolved iron and manganese than lake water. The sampling sites are located north of Florianópolis, Santa Catarina, Brazil.

2.1. Coagulation

Polyaluminum chloride (PAC) was chosen as a coagulant, seeking a compromise between the quality of treated water, no use of alkalization or acidification, production of small amounts of sludge, good handling conditions, preparation, and no temperature dependence.

The previous coagulation step was developed in a Nova Etica Model 218 jar test. The optimum PAC dosage was selected by constructing coagulation diagrams for UV absorbance at 254 nm removal and apparent color remaining as a function of the pH values and coagulant dosage.

From the results of the coagulation diagrams, the optimum conditions for rapid mixing and flocculation (time and velocity gradient) for the lake water were evaluated, and with the selected rapid mixing and flocculation conditions, PAC dosages for surface water and groundwater were adjusted.

2.2. Membrane filtration

The filtration experiments were conducted in a Koch membrane system LABCELL CF-1 type dead end-flow, flat cell, lab-scale unit operating in a batch mode, with a vessel of 500 ml of capacity and that provides an effective filtration area of 28 cm^2. The schematic design of the lab-scale equipment is shown in Fig. 1. The working temperature was set at 25°C and controlled with a thermostatic bath. The permeate volume was determined by weighing the collected volume using an analytical balance and converting it to the corresponding volume in liters.

Two types of membranes were tested: ROGA CA UF membrane and SELRO® MPF-36 NF membrane made by Koch Membrane Systems. The characteristics of the membranes are shown in Table 1. Each test was performed with a new membrane with previous conditioning (submersion in ultrapure water for ROGA CA membrane and caustic wash for SELRO® MPF-36 membrane), followed by compaction with ultrapure water for stabilization of the permeate flow. The permeate flux was calculated using following equation:

$$J = \frac{1}{A} \times \frac{dV}{dt} \tag{1}$$

where J is the flux membrane ($L\,m^{-2}\,h^{-1}$), A is the membrane area (m^2), V is the volume of filtrate (L), and t is the time (h).

To establish the operation pressure for the test, the hydraulic permeability for each membrane was calculated through Eq. (2). The hydraulic permeability of membranes was determined at pressures between 2 and 6 bar for the UF membrane, and pressures from 4 to 12 bar for the NF membrane, using ultrapure water and controlling temperature at 25°C.

$$K = \frac{J}{\Delta P} \tag{2}$$

where K is the hydraulic permeability ($L\,m^{-2}\,h^{-1}\,bar^{-1}$), J is the flux membrane ($L\,m^{-2}\,h^{-1}$), and P is the pressure (bar).

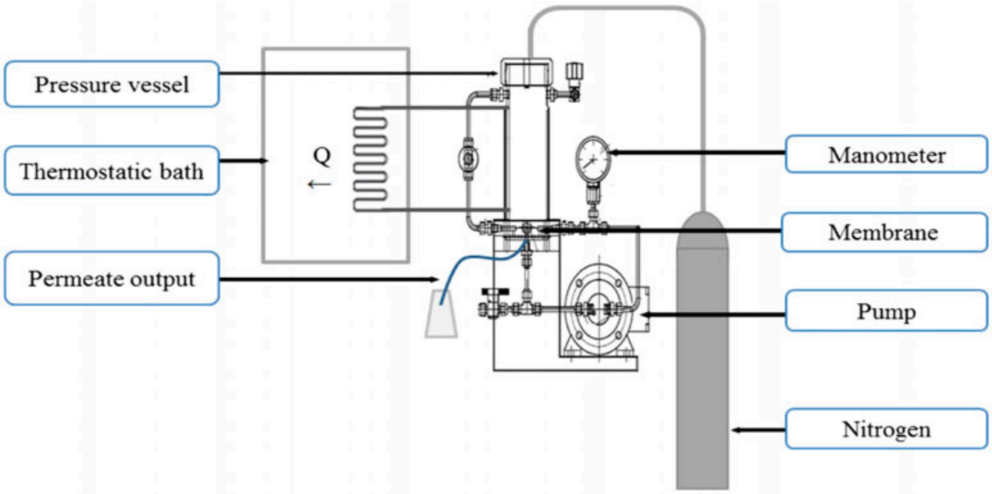

Fig. 1. Schematic diagram of the lab-scale filtration equipment with flat membranes.

Table 1
Characteristics of the membranes

	ROGA CA-UF	SELRO® MPF-36
Type	Ultrafiltration	Nanofiltration
Material	Cellulose acetate	Plastic patented material (Proprietary)
Molecular weight cutoff	8,000 Da	1,000 Da
Operation pressure	3.45 bar (Typical)	15–30 bar (Recommended)
	10.3 bar (Maximum)	35 bar (Maximum)
pH in continuous operation	3–7	1–13
Maximum temperature	40°C	70°C

Note: From: Koch Membrane Systems Catalog.

The operation pressures for the membranes were selected to get filtration periods near to 1 h for NF membranes and maximum 4 h for UF membranes. For operation, the vessel was filled with the study water, and the operation pressure was achieved by opening of the nitrogen valve.

2.3. Determination of the concentrations of pollutants

A Shimadzu TOC analyzer, model TOC-LCSH, was used to determine the dissolved organic carbon (DOC) in water samples, and a Hach Model 5000 UV–Vis spectrophotometer was used to measure the absorbance at 254 nm. A Hach model 2100P turbidimeter was utilized to determine the turbidity.

The colorimetric Ferrozine method with Hach® kits was applied to determine the total iron in the range of 0.000–1.300 mg L^{-1} with 0.009 mg L^{-1} accuracy. The colorimetric method 1-(2-pyridylazo)-2-naphthol with Hach® kits was utilized for manganese measurements in the range of 0.000–0.700 mg L^{-1} with 0.006 mg L^{-1} accuracy. A Hach model 2010 spectrophotometer was used for this purpose.

2.4. Raw water

The characteristics of the study waters are shown in Table 2. The values of DOC for surface water correspond to the commonly reported results for this type of source from 1.5 to 20 mg L^{-1}; the content of DOC in the groundwater, 17 mg L^{-1}, was higher than in surface water and exceeded the typical values for this parameter in this type of water found between 0.2 and 15 mg L^{-1} [10].

These contents of organic matter in the water may be due to the nature of the region, originally consisting of mangroves, which are ecosystems with high levels of organic matter. The organic matter was most likely transported from the soil to the groundwater through runoff by rainfall, [9] resulting in high contents of HS in the samples.

The low specific ultraviolet absorbance (SUVA) values (4.56 L mg^{-1} m^{-1} for surface water and 4.26 L mg^{-1} m^{-1} for groundwater) indicate, with respect to the predominance of fulvic acids in water, that it contains organic compounds of low molecular weight with high hydrophilicity and low aromatic content [1].

Table 2
Raw water characteristics

Parameter	Surface water	Ground water
pH	7.54	7.70
Apparent color (uH)	205	217
Turbidity (uT)	13.05	16.50
Dissolved iron (mg L^{-1})	0.237	0.784
Dissolved manganese (mg L^{-1})	0.018	0.199
Aluminum (mg L^{-1})	0.01	0.01
DOC (mg L^{-1})	13.20	17.48
Absorbance $UV_{254\ nm}$	0.602	0.744
SUVA (L mg^{-1} m^{-1})	4.56	4.26

The WHO guide indicates the limit for manganese and iron in drinking water of 0.1 and 0.3 mg L^{-1} to avoid undesirable taste and staining of sanitary ware and laundry [23]. The lake water values fall within the indicated values for potable water applications; however, the groundwater values exceeded the limits established, requiring a treatment to remove these compounds effectively.

3. Results and discussion

3.1. Coagulation

The coagulation diagrams for remaining apparent color and UV absorbance at 254 nm removal are shown in Fig. 2. HS removal may be presumed to occur primarily by drag, with the addition of larger quantities of the coagulant being necessary to cause rapid precipitation by drag of the aluminum hydroxide. The predominance of aquatic HS with low molecular weights that have higher oxygen contents causes a high density of negative charges that remain dispersed, [24] hindering the coagulation and requiring additional quantities of PAC to achieve apparent color and UV absorbance at 254 nm removal.

After coagulation diagram construction, the adjustment of the coagulation and flocculation conditions leads to rapid stirring for 10 s at a velocity gradient of 340 s^{-1} followed by 20 min of slow mixing at a velocity gradient of 12 s^{-1} and a sedimentation period of 30 min. Lower PAC dosages were selected according to these enhanced conditions and were 125 mg L^{-1} for surface water and 200 mg L^{-1} for groundwater.

3.2. Membrane filtration

The hydraulic permeabilities of UF and NF membranes are presented in Fig. 3. The operation test pressures of 4 and 8 bar were selected for the UF and NF membranes tests, respectively.

3.3. Removal efficiency for surface water and groundwater

Table 3 presents the values for the evaluated parameters in raw water, water after sedimentation, and water after sedimentation plus UF/NF for surface water and groundwater. Figs. 4 and 5 show the removal efficiencies for the parameters.

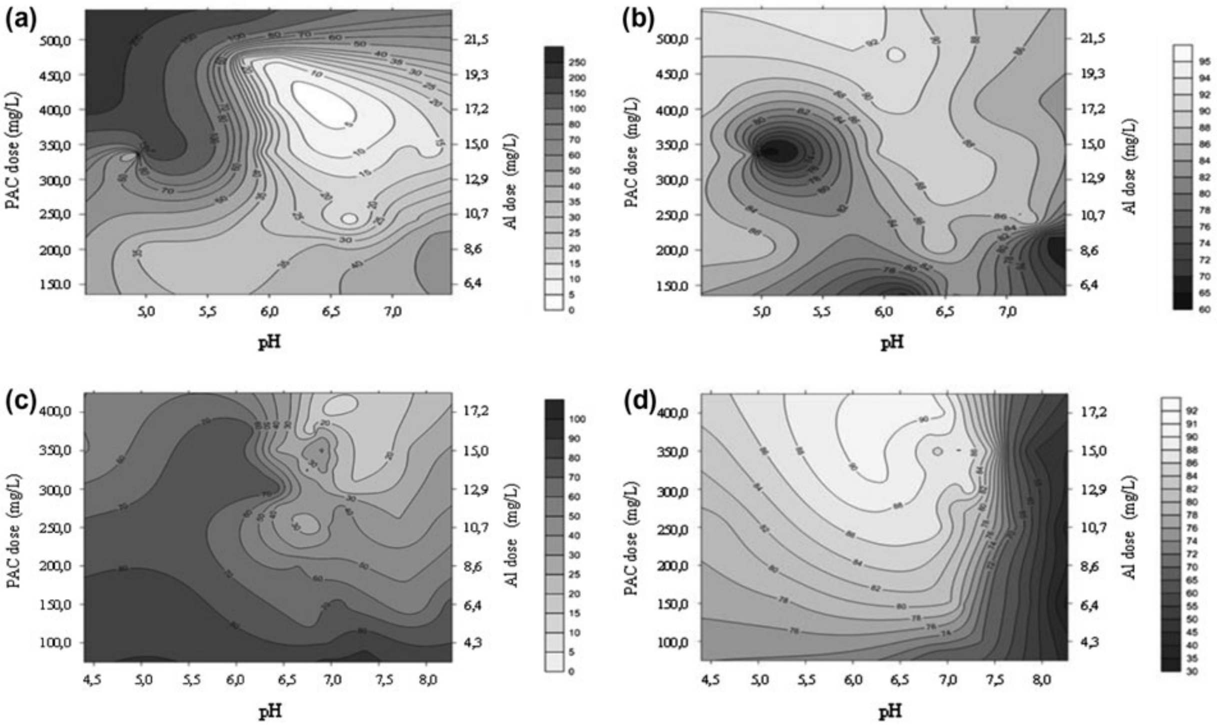

Fig. 2. Coagulation diagrams (rapid stirring for 60 s at a velocity gradient of 340 s^{-1} followed by 10 min of slow mixing at a velocity gradient of 48 s^{-1} and a sedimentation period of 30 min) (a) UV absorbance at 254 nm removal in surface water, (b) Apparent color removal in surface water, (c) UV absorbance at 254 nm removal in groundwater, and (d) Apparent color removal in groundwater.

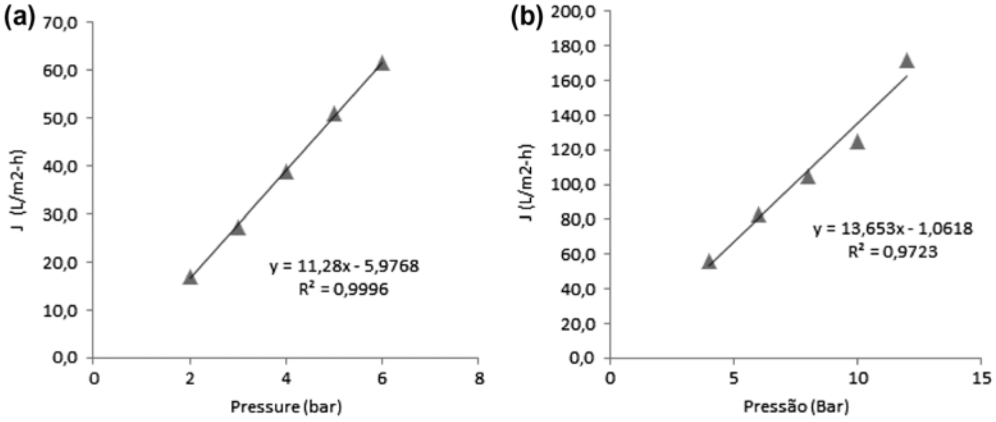

Fig. 3. Flux permeate (L m^{-2} h^{-1}) as a function of pressure (bar) at 25°C. (a) UF membrane and (b) NF membrane.

Surface water and groundwater show a decrease in the content of HS in the coagulation, flocculation, and sedimentation step. In terms of UV absorbance at 254 nm, HS removal in surface water achieved 72% and groundwater achieved 80%. In terms of DOC, the HS removal was 49% in surface water and 64% in groundwater. At this stage, this removal is mainly attributed to adsorption and enmeshment in aluminum hydroxide, considering the pH values of the samples. The presence of higher concentrations of iron in the groundwater contributes to the removal of HS from water, by precipitation of metal–HS complexes or by its absorption in the precipitated hydroxide particles [25] (Table 3).

With the passage through the UF and NF membranes, there was a considerable reduction in the remaining organic matter content. After UF, DOC values of 2.78 mg L^{-1} in surface water, corresponding to 79% HS removal, and values of 3.26 mg L^{-1} in groundwater, equivalent to 81% HS removal, were achieved. With NF, DOC values of 1.54 mg L^{-1} in surface water (88% HS removal) and values of 1.30 mg L^{-1} in groundwater (92% HS removal) were achieved, in accordance with the greater ability of the NF membranes to remove organic matter.

The differences between the iron and manganese removals are attributed to variations between the configuration and the stability of the complexes formed by each of these elements and humic compounds present in the water. The manganese was slightly complexed by HS in contrast to iron that is highly complexed by HS in aqueous systems.

PAC coagulation followed by flocculation and sedimentation was found to promote almost total removal of iron, obtaining final values of this element of less than 0.001 mg L^{-1} for the two types of water studied. The removal is probably due to the formation of aggregates between HS and the iron present in the water, leading to direct precipitation of the complex iron–HS formed or to the adsorption of the complex iron–HS onto precipitated aluminum hydroxide. Park and Yoon [22] reported the formation of the iron–HS complex when two or more coordination positions of the humic acid donor groups are occupied by the iron, thus forming a spherical structure. This configuration provides high stability to the complexes, as confirmed by the high stability constant reported [3]. Some authors report almost complete removal of iron using UF directly and combined with PAC as coagulant [26].

In the case of dissolved manganese, the coagulation, flocculation, and sedimentation stages did not contribute to its removal and, in treated water after NF, the removal was approximately 50%, whereas after UF, the removal was only 27%. This condition is due to the low capacity of formation of complexes between manganese and HS and the low stability of the formed complexes, impeding this phenomenon to contribute to the precipitation in the pretreatment or retention in subsequent filtration of this element. Barriquello et al. [27] studied the formation of complexes between HS and Mn^{2+}, and they observed the formation of aggregates with a conical shape (unlike the spherical particles present on iron complexes) and a large number of dispersed particles. The lower stability constants of the complexes of manganese and HS [3] indicate that a large fraction of Mn^{+2} is free.

Some authors indicate that with pH between 4 and 9, aluminum competes with other metal ions present in the formation of bonds with humic matter, establishing that this element has a higher complexing capability and forms more stable bonds with HS than manganese [28,29]. When the PAC is added in the

Table 3
Values of the evaluated parameters in raw water, water after sedimentation, and water after sedimentation plus UF/NF for surface water and groundwater

	Surface water				Ground water			
Parameter	Raw water	After sedimentation	After sedimentation + UF	After sedimentation + NF	Raw water	After sedimentation	After sedimentation + UF	After sedimentation + NF
pH	7.54	7.40	7.74	7.76	7.70	7.55	8.03	7.98
Apparent color (uH)	205	37	5	1	217	11	4.75	1
Turbidity (uT)	13.05	1.85	0.09	0.09	16.50	1.32	0.15	0.13
Dissolved iron (mg L^{-1})	0.237	0.001	0.001	ND	0.784	0.001	0.001	0.001
Dissolved manganese (mg L^{-1})	0.018	0.018	0.017	0.017	0.199	0.188	0.145	0.092
Aluminum (mgL^{-1})	0.01	0.43	0.04	0.02	0.01	0.25	0.08	0.02
DOC (mg L^{-1})	13.20	6.68	2.78	1.54	17.48	6.26	3.26	1.30
Absorbance UV_{254nm}	0.602	0.168	0.067	0.023	0.744	0.146	0.068	0.015
SUVA (L mg^{-1} m^{-1})	4.56	2.51	2.39	1.49	4.26	2.34	2.09	1.14

Note: ND: Not detected.

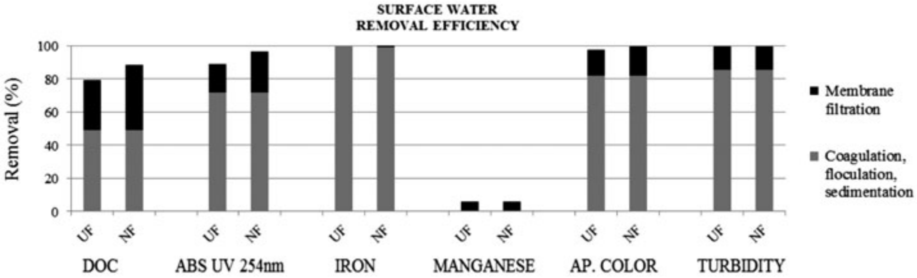

Fig. 4. Removal efficiency in surface water.

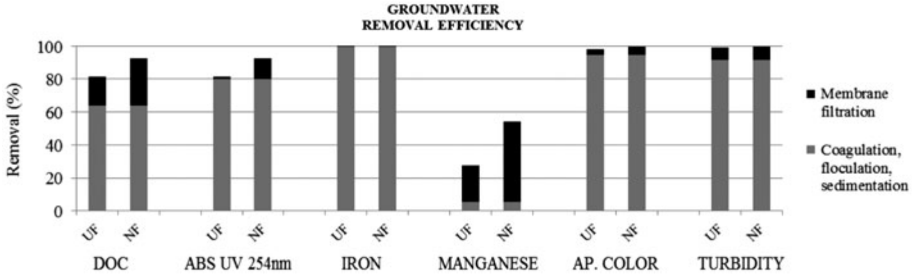

Fig. 5. Removal efficiency in groundwater.

coagulation step, aluminum can form complexes with the HS, displacing part of the complexed manganese, which is then found as free ion, which is not removed in the step of coagulation or in the UF and NF subsequently.

The measurement of the concentration of residual aluminum after the filtration membrane (UF and NF) confirms the retention of the residual aluminum present after sedimentation. In UF and NF, the final amount of aluminum present was less than 0.08 mg L^{-1}.

The two types of water studied are characterized by their low turbidity values (less than 20 NTU). As a result of the treatment with coagulation, flocculation, sedimentation, and filtration (UF/NF), the turbidity was reduced to less than 1 NTU. For the apparent color, using both pretreatment and membrane filtration for water greatly decreases these values with a removal efficiency between 97 and 99%. UF allows reductions to 5 uH, and NF reaches values of 1 uH for this parameter. Coagulation, flocculation, and sedimentation contribute to the removal of a large fraction of the apparent color and turbidity by reducing HS, iron, and particles, which reduces the deposition at the membrane surfaces, thus decreasing the fouling and improving the filtration performance.

3.4. Flux decreasing

A decrease in the permeate flux as a function of the operating time can be observed on both membranes used (UF and NF).

The fouling effect of NF membrane was more significant compared to the UF membrane. The tests showed approximately 15% of reduction of flux for NF membrane during the test and less that 5% for UF membrane during the test. This is in accordance with

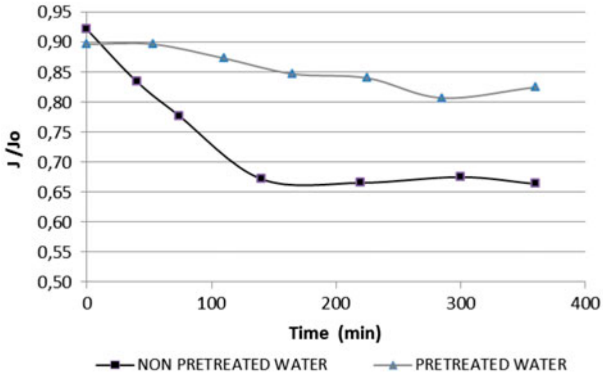

Fig. 6. Flux decreasing over time of filtering surface water with a NF membrane.

the greater retention of the lower cutoff molecular weights of NF membranes compared to UF membranes, complemented by the effect of a greater deposition of MON at the membrane surface caused by the higher pressures of the NF process.

Fig. 6 shows the results of the normalized permeate flux J/J_0 vs. time for the NF membrane using surface water. The total time of the test was 360 min. The initial ultrapure water flow was $113\,\mathrm{L\,m^{-2}\,h^{-1}}$ for pretreated water and $110\,\mathrm{L\,m^{-2}\,h^{-1}}$ for non-pretreated water. The decay of the raw water flow was approximately constant until a loss of slightly more than 30% of the ultrapure water flow after 120 min of operation and remained relatively stable over the remainder of the test. Moreover, pretreated water (coagulation, flocculation, and sedimentation) had an approximately constant decay for the initial 280 min of operation, with a loss of 20% of the initial ultrapure water flow; after this time, the water remained relatively stable during the test time.

The initial decrease of the flux observed in non-pretreated water can be attributed to the higher HS contents and, to a lesser extent, to the presence of iron, which are removed by the sedimentation stage and thus do not affect the filtration performance in the case of pretreated water.

The decrease in the flux of the pretreated water is possibly caused by the smaller fractions of HS not removed in the sedimentation process, as well as by other organic substances such as polysaccharides or proteins (which are a minority of natural organic matter), which cause irreversible fouling, according to some authors [30].

4. Conclusions

Considering the removal of contaminants and the permeate flow characteristics, filtration using NF membranes preceded by coagulation, flocculation, and sedimentation was presented as a good alternative for the treatment of water with a high content of low-molecular-weight HS, dissolved iron, and moderate concentrations of dissolved manganese.

Coagulation, flocculation, sedimentation, and UF/NF efficiently removed dissolved iron, HS, apparent color, and turbidity. However, the system did not appear effective (less than 50% removal) in removing dissolved manganese. To treat water with high amounts of manganese, it would be necessary to implement some additional processes, such as oxidation or adsorptive filtration with adequate adsorbent beds.

Coagulation, flocculation, and sedimentation stages as a pretreatment for UF and NF improve system performance by reducing the loss of filtration flow because of the removal of high-molecular-weight HS, thus minimizing the formation of fouling on the membrane.

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