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Humic acid removal by deep-bed filtration and by UF membranes

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ABSTRACT

Currently, rational choice of either the conventional filtration method or of the more expensive membrane pretreatment technique is hampered by the lack of sufficient experience and the paucity of design data. The main objective of the present study was to compare water qualities achieved by filtration of humic acid feed solutions by the two alternate pretreatment techniques under well controlled conditions. Deep-bed filtration of humic acid in the presence of the coagulant ferric chloride was performed in a continuous flow column (98 mm diameter, 750 mm long) filled with silica sand grains of 0.65 mm. Two PVDF tubular UF membranes were tested — a large pore size membrane of 100 kDa and a small pore size membrane of 20 kDa. In both systems, commercial humic acid solutions were tested at feed concentrations covering the range of 5–50 ppm. Water quality was monitored by TOC and turbidity measurements. Meaningful interpretation of conflicting water quality data was obtained by interlinking TOC and turbidity removal measurements with the particle size distribution of the feed solution. One of the main results of this study is that in the case of humic acid removal, both pretreatment techniques appear to be capable of providing substantially identical product qualities.

Keywords: Pretreatment; Deep-bed filtration; Granular medium; Ultrafiltration; Humic acid

1. Introduction

The single most significant challenge in seawater and wastewater reverse osmosis (RO) desalination is effective pretreatment. A crucial requirement for trouble free and cost effective desalination is a pretreatment system providing consistently a well-filtered foulant-free feed to the RO system. Pretreatment has a pronounced impact on process economics; pretreatment related costs may reach as much as 10–20% of the plant capital cost.

Conventional deep-bed filtration has a proven track record as part of pretreatment processes used in RO desalination of both saline and brackish feed waters. With seawater feeds, it is usual to enhance the filtration process by dosage of a coagulating agent. The advent of microfiltration (MF) and ultrafiltration (UF) membranes opened possibilities for developing alternative pretreatment techniques based on these low pressure membranes. The potential benefits of membrane pretreatment processes stemming from the improved pretreated water quality are claimed to be [1,2] in increased permeate flux rates, longer RO membrane life, reduced RO membrane cleaning costs, lower energy costs and reduced plant footprint size. However, UF/MF systems, may suffer from severe fouling problems which are less common in deep-bed filters.

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Currently, rational choice of either a conventional or the more expensive membrane pretreatment system is hampered by the lack of sufficient experience and inadequate technical know-how. The main objective of the present study was to compare water qualities achieved by filtration of a model foulant by the two alternate pretreatment techniques under well controlled conditions. Some of the critical parameters involved in the comparative evaluation of the two pretreatment technologies were examined by well controlled experiments.

The choice of a model foulant is clearly of central importance for investigating alternate pretreatment methods. The main issues considered in the selection of a model foulant were:

- Reasonably well characterized
- Readily analyzed
- Commercially available
- Of practical importance in water treatment operations

A foulant meeting these considerations is humic acid. Humic substances are found in soils and waters. Their origin is the decomposition of plant and animal tissues and yet, they are more stable than their precursors. Humic materials vary in their composition, structure, molecular weight, number and position of functional groups (depending on their origin and age) but their similarities are more pronounced than their differences.

Traditionally, humic substances are classified into three main categories, differing by their solubility in water:

- fulvic acids which are soluble at all pH values
- humic acids which are insoluble at acidic pH values (pH < 2) and soluble at higher pH levels
- humins which are insoluble at all pH values

Humic materials elemental composition is approximately 40–60% carbon, 30–50% oxygen, 4–5% hydrogen, 1–4% nitrogen, 1–2% sulphur and 0–0.3% phosphorus (humic acids contain more H, C, N and S and less O than fulvic acids). The ranges of molecular sizes for the majority of humic acids place them in the colloidal range in aqueous solutions. Humic concentration, pH and ionic strength control the colloidal structure. At high concentrations (> 3.5 g/L), low pH (< 3.5) and high ionic strength (> 0.05 M), humic materials are rigid uncharged colloidal particles. At low concentrations, high pH and low ionic strength, humic materials are flexible linear polyelectrolytes.

2. Experimental

2.1 Deep-bed filtration system

The filtration system (Fig. 1) consisted of a continuous flow vertical column (internal diameter of 98 mm) filled with silica sand grains having an average size of 0.65 mm; the silica bed was held on a 25 cm basalt supporting layer. The feed solution consisted of tap water mixed with technical grade HA sodium salt, supplied by Sigma-Aldrich. The HA concentration range studied was 5–50 ppm. The solution pH was set to 5.0 using hydrochloric acid. Inline coagulation with ferric chloride (hexahydrate puriss. p.a., Fluka Chemicals) was undertaken. Fe concentrations ranged from 1 to 10 ppm.

Filtrate turbidity and TOC concentration were periodically monitored. Turbidity was measured with HACH turbidimeter, model 2100P. TOC concentration was determined using Multi N/C 2100/2100 analyzer,

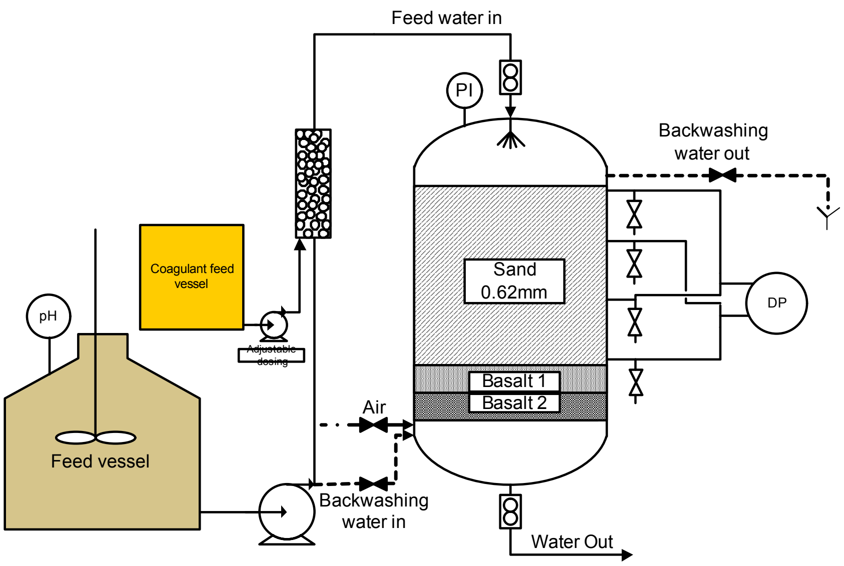

Fig. 1. Deep-bed filtration system.

Analytik Jena. The feed solution particle size distribution was characterized with model LS230 Coulter analyzer.

Filtration experiments were conducted in a constant flow mode of operation. The flow velocity was in the range of 5–15 m/h. Cleaning of the bed at the end of an experiment was performed by a backwash with aerated fresh water followed by HA removal with caustic soda (0.07 M), water rinsing and a bleaching solution (1 g/L) backwash.

2.2. Ultrafiltration system

The ultrafiltration system consisted of a UF tubular membrane (ITT PCI membranes, 12.5 mm diameter, 2×300 mm long). Two PVDF tubular membranes were tested — a large pore size membrane of 100 kDa and a small pore size membrane of 20 kDa. The membranes were held inside a stainless steel housing (MIC-RO 240).

The feed solutions tested contained 5 to 50 ppm HA and were set to a pH of 7.0. No coagulants were dosed. To prevent bacterial growth, feed solutions were dosed with 0.04% wt of the biocide sodium azide (GR, Loba Chemie).

The membrane filtration experiments were conducted in a cross flow mode of operation at a constant pressure in the range of 15–45 psi and a constant concentrate flow velocity in the range of 10–100 cm/s. Feed solution particle size distribution was characterized using Malvern Nanosizer device, model Nano-ZS. Periodic measurements monitored during an experiment were permeate flux, pH and TOC of the feed solution and of the permeate. Membrane cleaning at the end of an experiment was performed by circulating a caustic solution mixed with a detergent at a pH 10 followed by water rinsing.

3. Water quality criteria for assessing pretreatment effectiveness

3.1. Characterization of water qualities achieved by different pretreatment techniques

A major factor in the evaluation of the relative effectiveness of different pretreatment techniques is assessment of the product water quality. A complicating issue is that different entities are used to characterize water quality; as demonstrated below, water quality trends indicated by different entities do not always coincide. Development of standardized water quality criteria would greatly facilitate rational comparison of the relative effectiveness of different pretreatment techniques.

The main parameters commonly applied for characterizing the water quality achieved by either deep-bed filtration or membrane pretreatment are as follows:

Turbidity: Turbidity is determined by the intensity of light scattered by the suspended particles present in a solution and is expressed in NTU units. One NTU unit is defined as the intensity of light scattered by a solution containing 1 ppm of a reference suspension. Turbidity is an easily measured parameter but it provides a rather crude indication of the level of suspended solids.

Total suspended solids (TSS): TSS represents the concentration of suspended particles retained by a filter of 0.45 μm.

Total dissolved solids (TDS): TDS represents the concentration of dissolved matter in a solution.

Total organic carbon (TOC): TOC represents the carbon content of organic matter in a solution. It is determined by measuring the CO_2 effluent formed in complete oxidation of the organic matter.

Silt density index (SDI): The SDI of a solution is a measure of the decline in filtration rate due to filter clogging in the course of a standardized filtration protocol (ASTM D 4189-95). The fouling occurring in an SDI test is formed by dead-end flow whereas fouling in RO systems is usually formed under cross flow conditions. SDI provides a crude indication of the level of suspended colloidal particles but is widely used to characterize the fouling propensity of feed waters.

UV light absorption: Light absorption measurements in both the ultraviolet range (254 nm) and the lower part of the visible range (400–600 nm) are often applied for simple quantification of organic compounds content in water. The absorption of light at these wavelengths is due to the presence of aromatic rings, to conjugated unsaturated bonds and to the presence of free electron pairs on heteroatoms.

3.2. Demonstration of discrepancies in water quality characterizations

The parameters listed above have the advantage that there they are relatively easy to measure and are therefore widely used to characterize water quality. However, quantitative comparison of data measured by different parameters often yields conflicting results, as illustrated below.

3.2.1 Correspondence of SDI and turbidity measurements

In their study of the sensitivity of SDI analyses, Mosset et al. [3] provide an example showing discrepancies between SDI and turbidity data of pretreated feed water measured during six months (Fig. 2). It is seen that while the turbidity level was low (0.2–0.3 NTU) and remained constant throughout the test period, the SDI level significantly increased, from 0.4 to 1.8.

Another example illustrating an inconsistency between turbidity and SDI measurements is found in results reported by Ando et al. [4]. SDI and turbidity tests were carried out on two types of filtrate using the same seawater. The filtrate produced by a UF membrane had a very low turbidity level of 0.001 NTU and a relatively high SDI level of 4.0%/min. The filtrate produced by a dual media filter had a higher turbidity level of 0.01 NTU but a lower SDI level of 2.7%/min.

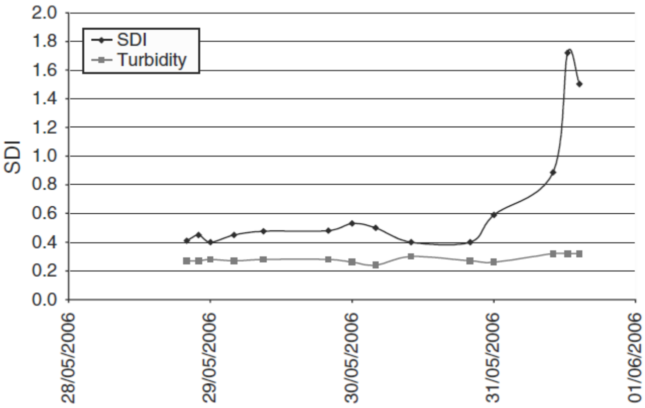

Fig. 2. SDI and turbidity measurements of pretreated feed water [3].

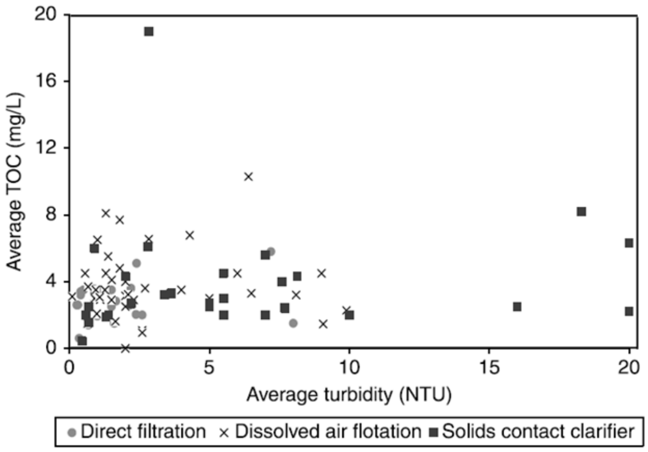

Fig. 3. Average levels of TOC and turbidity measured in different treatment plants [5].

3.2.2. Correspondence of turbidity and TOC measurements

An inconsistency between measurements of TOC and turbidity is clearly displayed in data reported by Valade et al. [5]. These authors analyzed feed water characteristics of 400 US treatment plants and provided guidelines for proper selection of a technique for NOM removal. Fig. 3 shows average values of TOC and turbidity measured in the product of three different treatment plants operated by direct filtration, dissolved air flotation (DAF) and solid contact clarification respectively. It is seen that the TOC level does not correspond to the turbidity level and that water with a high TOC level can have either a low or a high turbidity level. Similar inconsistencies were observed in the comparison of color and turbidity data as well as turbidity and UV_{254} measurements.

3.3. Characterization of "filtration cut"

3.3.1 The "cut" of a filter medium

A rational technique for characterizing a filter separation capability was developed in this study by interlinking the TOC and turbidity removal measurements with the size distribution of the particles in the feed solution. The basic premise is that the TOC removal level is governed by the size distribution of the particles. The percentage TOC passage through the filter medium can thus serve to identify the "filter bed cut", i.e. the limiting size of particles that cannot be captured by the bed.

The "cut" evaluation method, based on both TOC and turbidity measurements, is illustrated in Fig. 4 for Run H28. The feed TOC was 5.8 ppm and the filtrate TOC was 3.6 ppm indicating that 62% of the particles passed through the filter medium. The cumulative size distribution measured by the Coulter Instrument showed that the limiting particle size corresponding to 62% cumulative particle volume is 35 μm. The analysis thus indicates a filter "cut" of 35 μm, i.e. particles smaller than 35 μm pass through the filter while particles larger than 35 μm are captured inside the medium. Evaluation of the filter "cut" from TOC measurements of numerous tests [6] covering a wide range of operating conditions (feed HA 5–50 ppm, feed Fe 3–13 ppm, filtration rate 7–12 m/h), yielded a substantially constant filter "cut" value of 25.2±2.6 μm.

Evaluation of the filter "cut" from turbidity data gave far less consistent results. This is to be expected since, as mentioned above, the link between turbidity and particle size is very indirect. The feed turbidity in Run H28 was 9.7 NTU and the filtrate turbidity was 0.48 ppm indicating a 5% passage of the particles through the filter medium. The corresponding separation "cut" from the particle size distribution plot is 11 mm. Analysis of turbidity data of numerous tests yielded a filter "cut" value of 8.9±1.5 μm. The low level of this "cut" is beyond the usual separation ability of conventional sand filters. It seems therefore that filter medium characterization on the basis of turbidity data shoud be viewed with caution.

3.3.2 The "cut" of an ultrafiltration membrane

The same methodology was used to determine the separation "cut" of the UF membranes on the basis of TOC data and the particle size distributions measured by the Malvern nano-sizer. Since UF membrane tests were carried out without coagulant dosage, the HA in the feed solutions had an essentially constant size distribution, with only a minor effect of the concentration level.

The "cut" evaluation method for a UF test is illustrated in Fig. 5 for Run U15. The TOC data indicated a 50% passage of the HA through the membrane. The size distribution identifies a membrane separation "cut" at this passage ratio of 250 nm, i.e. the membrane rejected particles larger than 250 nm and allowed passage of particles smaller than 250 nm.

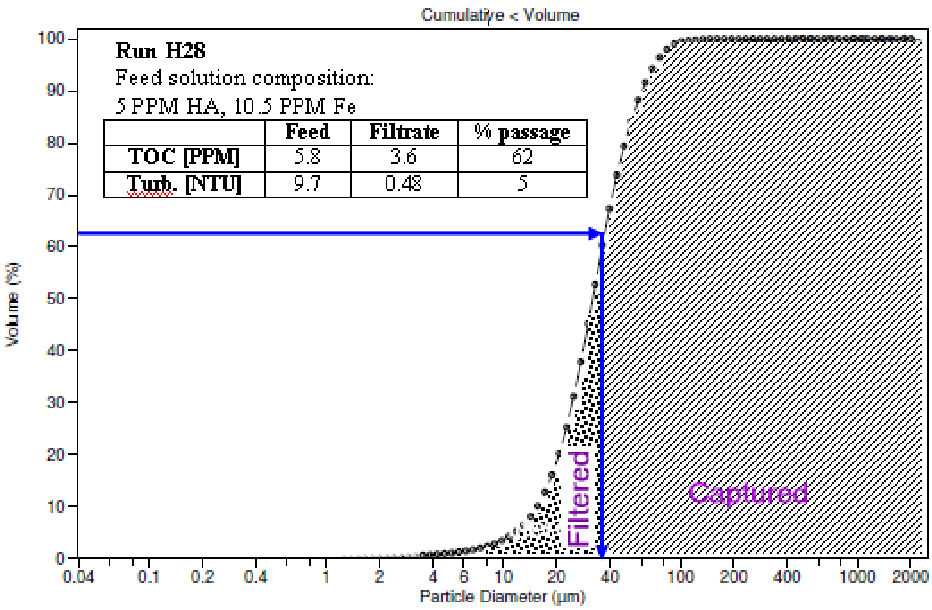

Fig. 4. Illustration of the "cut" evaluation method for a sand filtration test (run H28).

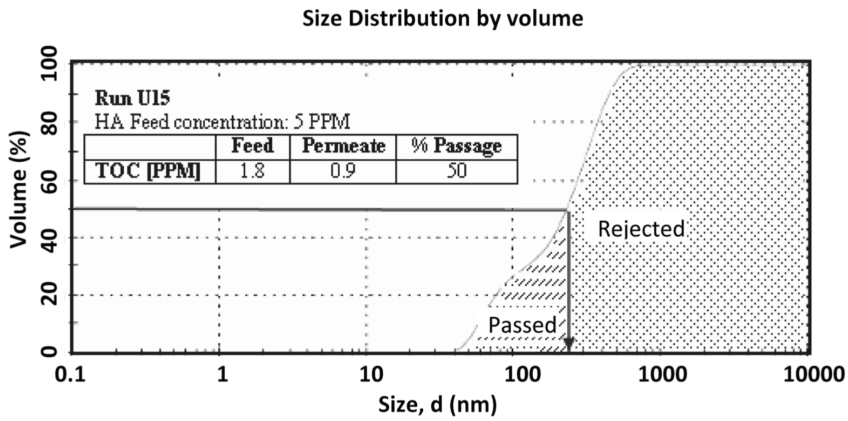

Fig. 5. Illustration of the "cut" evaluation method for a UF test (run U15).

Tests covering a rather wide range of conditions (HA feed concentrations of 5–50 ppm, flow velocity of 15–140 cm/s) were conducted to characterize the filtration cut"of two UF membranes — PVDF 100 kDa and PVDF 20 kDa membrane [6]. The TOC data indicated that the larger pore size membrane (PVDF 100 kDa) had a separation "cut" of 212±46 nm. As expected, the smaller pore size membrane (PVDF 20 kDa) had a lower separation "cut" of 140±18 nm. These "membrane cut" values are within the expected rejection levels of UF membranes.

4. Water qualities achieved by deep-bed filtration

4.1. Deep-bed filtration of humic acid

The removal of particles by deep-bed filtration involves several complex mechanisms. Particle removal is achieved by both particle transport to the medium grains and particle attachment to the grains. Therefore, all factors that affect particle transport and attachment are expected to affect filtrate quality. Suspension concentration, coagulant type and dosage and flow velocity are the main factors that are likely to influence filtrate quality.

The effect of various parameters on filtrate quality was investigated in a series of experiments covering the following range of operating parameters: HA feed solution concentration from 5 to 40 ppm, Fe feed solution concentration from 3 to 13 ppm as Fe and filtration flow velocity from 7 to 12 m/h (Table 1).

4.1.1. Effect of HA feed solution concentration

The effect of HA feed solution concentration on filtrate quality was studied in 3 sets of experiments in

Table 1
Effect of HA feed solution concentration on the filtration efficiency of the deep bed filter

Set	Run	Velocity (m/h)	Fe conc. (ppm)	Feed solution characteristics			% Turbidity removal	% TOC removal
				HA conc. (ppm)	Turbidity (NTU)	TOC (ppm)		
I	H16	10	3–4	10	16.8	6.3	98	63
	H11			20	15.6	8.5	71	52
II	H29	8.2	7	5	10.2	5.1	92	43
	H33			10	33.0	7.2	99	60
III	H27	10	5	5	7.3	5.0	97	44
	H17			15	17.2	9.6	94	64

which HA feed solution concentration was varied while flow velocity and coagulant dosage were kept constant. Filtrate quality was characterized by turbidity and TOC measurements.

All runs exhibited gradual improvement in filtrate quality during the initial so-called "ripening period". This is illustrated in Fig. 6 which shows the change in filtrate quality as a function of filtrate volume in set I runs conducted at HA feed concentrations of 10 and 20 ppm (Table 1). It is seen that in the 10 ppm run, the filtrate TOC content decreased in the "ripening period" from 5 to 2 ppm while filtrate turbidity also decreased from 8 to 4 NTU. Similarly, in the 20 ppm run, the filtrate TOC content decreased in the "ripening period" from 17 to 4 ppm while filtrate turbidity decreased from 12 to less than 1 NTU.

Results on the effect of HA feed solution concentration on the TOC and turbidity removal efficiencies are summarized in Table 1. The data do not reveal a clear trend.

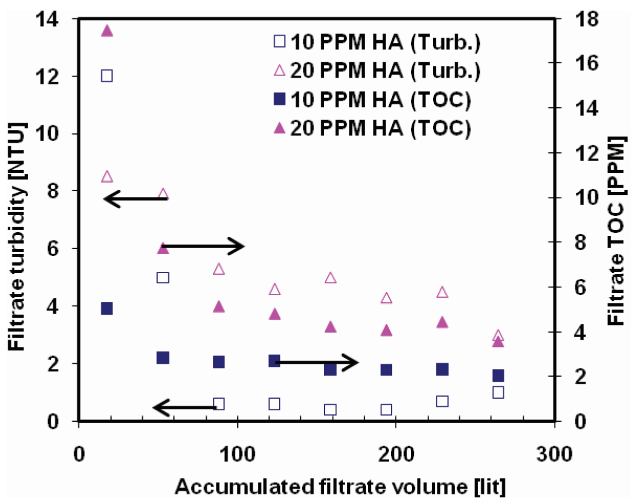

Fig. 6. Filtrate turbidity and TOC content as a function of total filtrate volume at two HA feed concentrations.

In set I increase of the HA feed concentration reduced both the turbidity and TOC removal efficiencies. In set II the trend is reversed — both turbidity and TOC removal efficiencies increased when HA feed concentration was augmented. In set III, increase of HA feed concentration decreased the turbidity filtration efficiency but increased the TOC filtration efficiency. It appears therefore that the effect of HA feed concentration is interwoven with the effect of other parameters.

However, inspection of the data past the ripening period revealed an important result relating HA feed solution concentration to the TOC filtrate concentration. Fig. 7 displays filtrate TOC concentration as a function of HA feed concentration for runs conducted with either a new granular medium or a freshly cleaned bed. It is seen that up to a feed concentration of 20 ppm, the TOC content in the filtrate lies within a rather narrow range of 2.5–4 ppm, regardless of the HA feed concentration, the coagulant dose and the flow velocity level. The cleanliness level of the bed does not seem to have an effect on this result. Fig. 8 displays TOC filtrate results of all runs which include experiments with used beds prior to breakthrough

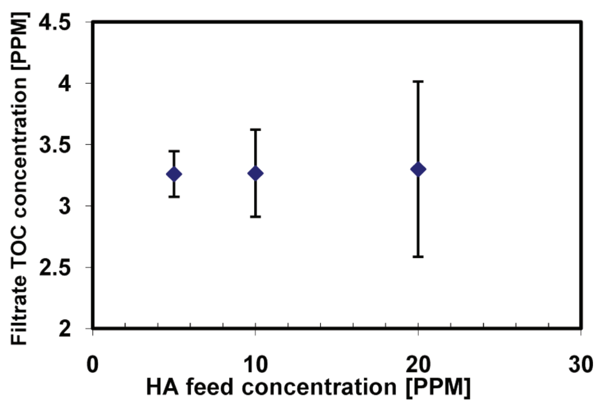

Fig. 7. Mean filtrate TOC content vs. HA feed concentration in filtrations performed in a fresh bed or in a cleaned bed.

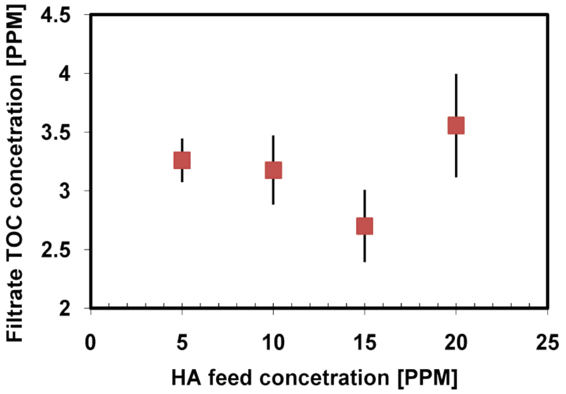

Fig. 8. Mean filtrate TOC content vs. HA feed concentration in filtrations performed in either a cleaned bed or a used bed.

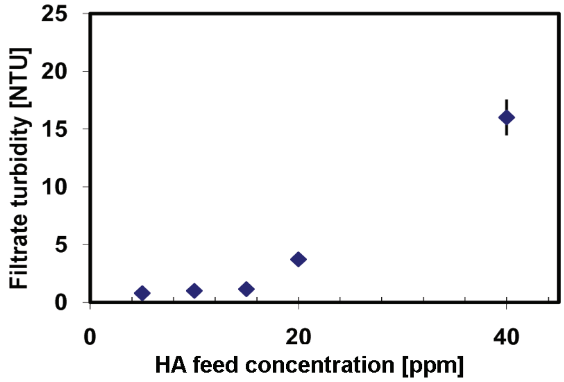

Fig. 10. Mean filtrate turbidity vs. HA feed concentration in all runs.

conditions. It is seen that the TOC content in the filtrate was essentially similar to that measured in clean beds.

As may be anticipated, the higher feed solution of 40 ppm resulted in much higher filtrate TOC levels at all filter conditions — fresh, cleaned or un-cleaned (Fig. 9). The insignificant change in the filtrate TOC up to a concentration of 20 ppm may be explained by one of the known filtration mechanisms consisting of gradual shift of the particle capture zone from the upper bed layers to the deeper layers as filtration progresses. Thus, as long as the particle solution concentration is not excessively high, the only effect of an increased concentration is an earlier breakthrough.

The turbidity results conformed to the trends displayed by the TOC data. As seen in Fig. 10, HA feed concentration induced a negligible effect on filtrate turbidity of 1 NTU in the range up to 20 ppm HA but caused a significant turbidity increase (up to 17 NTU) at the HA level of 40 ppm.

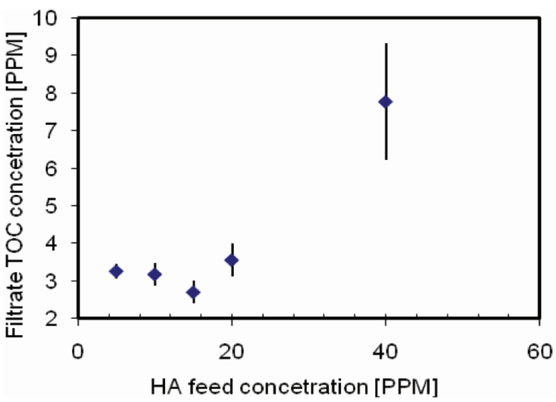

Fig. 9. Mean filtrate TOC content at all HA feed concentrations in all runs.

4.1.2. *Effect of coagulant (Fe) concentration*

Removal of NOM is influenced by the coagulant used, the coagulant dosage and the solution pH [7]. Increasing the coagulant dosage can either decrease abruptly the solution TOC to a final constant level (type I pattern) or result in a gradual reduction of the solution TOC level (type II pattern). Type I is indicative of precipitation and is associated with the more removable NOM species while type II is attributable to adsorption and is associated with the less coagulable species. The optimum pH is generally in the range of 5–6 [7]. As previously stated, all filtration tests were carried out at the pH of 5.

Table 2 summarizes the experimental conditions and the effect of the coagulant on filtrate quality. Fig. 11 displays measurements of the filtrate turbidity and TOC

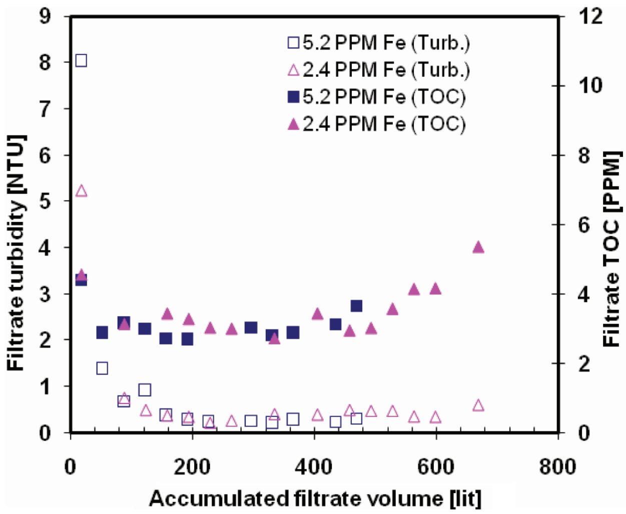

Fig. 11. Filtrate turbidity and TOC content vs. accumulated filtrate volume at two different Fe feed concentrations (set I runs).

Table 2
Effect of the coagulant feed concentration on the filtration efficiency of the sand filter

Set	Run	Velocity (m/h)	HA conc. (ppm)	Feed solution characteristics			% Turbidity removal	% TOC removal
				Fe conc. (ppm)	Turbidity (NTU)	TOC (ppm)		
I	H26	10	10	2.4	5.9	5.5	94	47
	H27			5.2	16.8	6.3	98	54
II	H33	8.2	10	7.3	34.5	7.2	99	60
	H34			2.7	35.6	7.3	98	63

content as a function of the cumulative filtrate volume in set I runs conducted at Fe levels of 2.4 ppm (Run H26) and 5.2 ppm (Run H27). HA feed concentration in both runs was 10 PPM and flow velocity was 10 m/h.

The data in Fig. 11 show that the ripening period was rather short. The TOC content declined from 5 to about 3.5 ppm in both runs. The turbidity declined from 5 to about 0.3 NTU in the 2.4 ppm Fe Run and from 8 to about 0.3 NTU in the 5.2 ppm Fe run. After the ripening period, values of filtrate turbidity and TOC content were practically identical at the two Fe levels. Also, the removal efficiencies of turbidity and TOC were substantially similar at the two Fe concentrations. The trends observed in set II runs were identical to those seen in set I. Again increase of Fe dosage had no effect on the filtration performance. These results clearly indicate that the coagulation followed type I pattern.

5. Ultrafiltration of humic acid

Membrane fouling by humic substances is a major problem in UF water treatment. Fouling is attributed to accumulation of particles in the feed water on the membrane surface forming a cake layer and adsorption of small particles into the inner pores thus constricting or blocking the pore mouth. The exact contribution of each of these mechanisms to the membrane fouling and to the flux reduction is not sufficiently clear .A comprehensive review of HS fouling [8] highlights the complexity of the phenomena involved. The extent of fouling is influenced by numerous parameters which include physico-chemical properties of the humic substances, membrane properties and hydrodynamic conditions.

The following sections present data showing effects of the membrane MWCO, the concentrate flow velocity, the HA feed solution concentration, and the permeation flux on the rate of flux decline and the HA rejection level.

5.1. Effect of membrane MWCO

One of the difficulties of studies aiming to investigate the effect of MWCO on HS fouling and rejection lies in the inadequate definition of the pore size distribution and of the overall membrane porosity of UF membranes. Virtually all studies aiming to evaluate the effect of the MWCO on HS fouling found that fouling is more severe in the more porous high MWCO membranes than in the less porous low MWCO membranes. However, most of these studies were conducted under identical applied pressures rather than under identical initial fluxes [9–14]. Such operating conditions are strictly not comparable since the higher permeation flux obtained with the more porous membrane is by itself a factor leading to enhanced transport of the fouling species towards the membrane.

The effect of membrane MWCO on permeate flux decline and on HA rejection was studied using two different PVDF membranes having MWCO values of 20 and 100 kDa The performance of the membranes was tested using the same initial permeate flux of 75 LMH, the same flow velocity of 15.8 cm/s and the same HA feed concentration of 40 ppm. Temperature of the water was 22°C.

Literature results measured under constant pressure conditions indicate a significant effect of MWCO. The data measured in this study under identical initial permeate fluxes show a minor effect. This is illustrated in Fig. 12 displaying the decline in permeate flux ob-

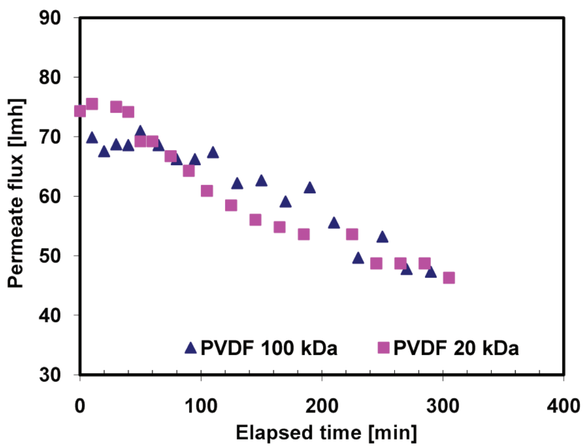

Fig. 12. Permeate flux as a function of time with high and low MWCO membranes.

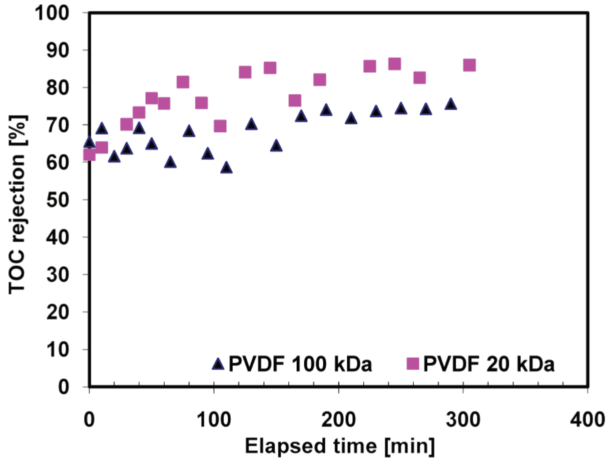

Fig. 13. TOC rejection as a function of time with high and low MWCO membranes.

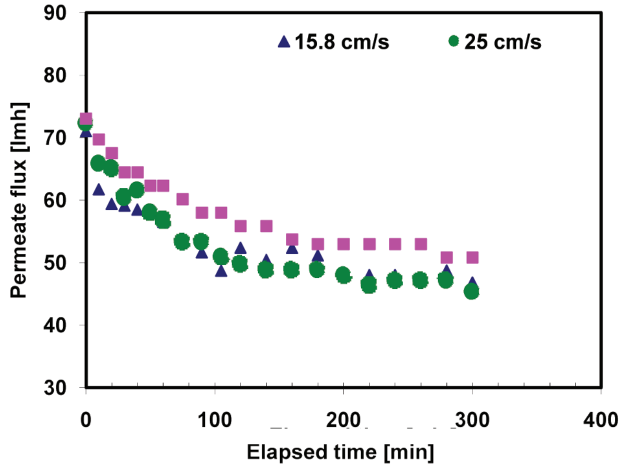

Fig. 14. Effect of flow velocity on permeate flux.

served in comparative experiments performed with the two membranes. In both runs, a permeate flux decline of 38% was measured. The rejection data displayed in Fig. 13 also show a minor effect of the MWCO. The TOC rejection of the low MWCO membrane was around 80% compared to a TOC rejection of about 70% for the high MWCO membrane.

5.2. Effect of flow velocity

The effect of flow velocity on permeate flux decline and on HA rejection was studied in three sets of runs (Table 3) performed at HA feed concentrations of 10, 20 and 50 ppm respectively. The runs were conducted with the PVDF 100 kDa membrane. Initial permeate flux was in the range of 70–80 lmh. The flow velocity was varied in the range of 15–50 cm/s. Each run lasted 300 min.

Fig. 14 shows the flux decline measured at three velocities with the lowest feed concentration of 10 ppm HA. The flux decline of 38% at the lowest flow velocity of 15 cm/s was somewhat reduced to 30% at the highest flow velocity of 40 cm/s Fig. 15 displays the corresponding TOC rejection data. The scatter in the data does not

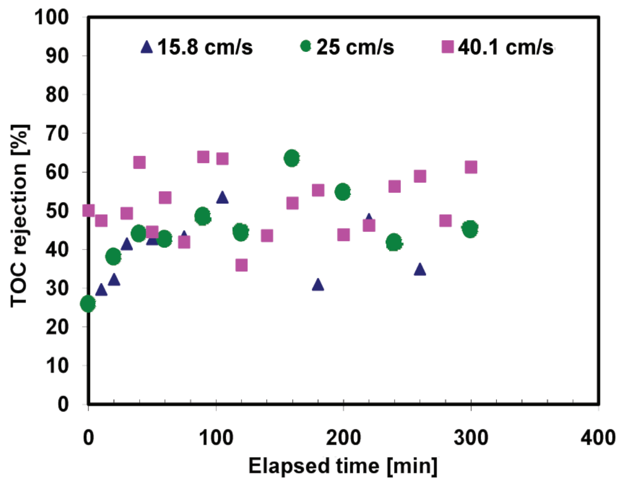

Fig. 15. Effect of flow velocity on TOC rejection.

Table 3
Effect of the flow velocity on flux decline and TOC rejection

Set	HA conc. (ppm)	Flux (lmh)	Temp. (°C)	Run No.	Velocity (cm/s)	Flux reduction in 300 min	TOC rejection
I	10	72	27	U28	15.8	38%	50±10%.
				U27	25.0	38%	50±10%
				U26	40.1	30%	50±10%
II	20	70	27	U22	31.7	32%	70%
				U30	79.8	32%	70%
III	50	80	22	U9	15.8	40%	60–75%
				U8	50.0	40%	75–85%

enable to discern an effect of the flow velocity. The TOC rejections at all velocities were around 50±10%.

The flux decline data and the TOC rejection results of the runs carried out in set II with a feed concentration of 20 ppm HA showed no effect of velocity. In all runs, the flux decline was around 32% and the TOC rejection, around 70%. The data measured in set III runs which were conducted at the highest feed concentration of 50 ppm HA also showed no velocity effect. In all runs, the flux decline was around 40% and the TOC rejection, around 75%.

Flow velocity is generally considered to be an important parameter influencing membrane flux and membrane fouling. The ratio of permeate flux J_v to the mass transfer coefficient k governs the concentration polarization level. At a low flow velocity, the relatively small value of k augments the concentration polarization modulus. This induces a relatively high concentration of the foulant on the membrane surface which acts to accelerate fouling. Increase of velocity reduces the accelerated fouling tendency and can have an additional beneficial effect. At a sufficiently high velocity, the shear stress on the membrane surface can dislodge a weakly adhering fouling layer. These trends were not observed in the three sets of experiments reported above.

5.3. Effect of HA feed solution concentration

The effect of HA feed solution concentration on permeate flux decline and on HA rejection was studied in runs covering a range of HA feed solution concentrations of 5–50 ppm. The trends observed are illustrated in Fig. 16 and Fig. 17 showing the effect of increasing the HA feed concentration from 5 to 20 ppm while maintaining an initial flux at a level of 75 lmh and the flow velocity at 86 cm/s. The tests were carried out at 25°C over a period of 300 minutes with the PVDF 100 kDa membrane.

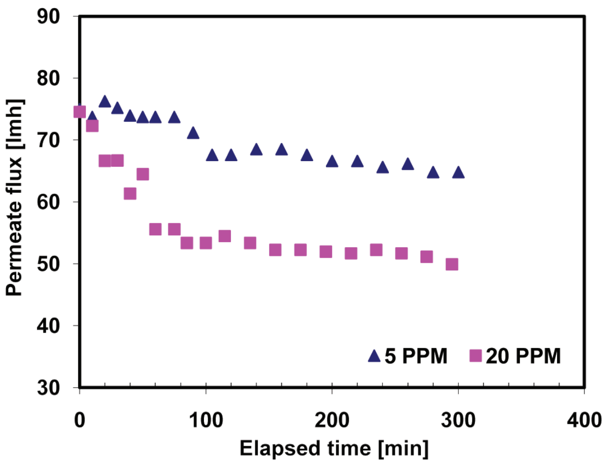

Fig. 16. Effect of HA feed solution concentration on the flux decline with time.

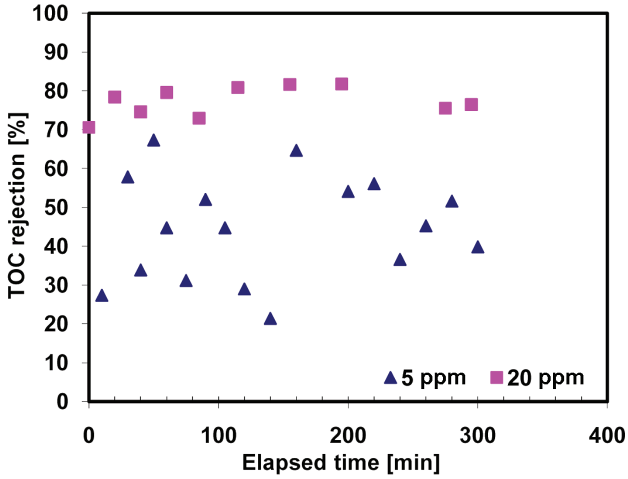

Fig. 17. Effect of HA feed solution concentration on the TOC rejection.

Fig. 16 displays data on the permeate decline with time. As anticipated, the higher HA feed concentration of 20 ppm induced a higher flux decline of 33% compared to a flux decline of 14% observed in the low feed concentration run.

Fig. 17 displays data on the TOC rejection. Rejection was significantly improved at the higher HA feed solution concentration — 80% rejection in the 20 ppm HA feed concentration run and 40±20% in the 5 ppm HA feed concentration run. A possible explanation for this result is that the higher flux decline at 20 ppm HA feed promoted a thicker cake layer enabling capture of a higher proportion of the HA particles.

5.4. Effect of initial permeate flux

The effect of initial permeate flux on flux decline and HA rejection was studied in three sets of runs (Table 4) performed at HA feed concentrations of 5, 20 and 50 ppm respectively. The runs were conducted with the PVDF 100 kDa membrane at a flow velocity of 86.3 cm/s. Initial permeate flux was varied in the range of 70–160 lmh.

The results summarized in Table 4 show that the initial permeate flow rate had a minor effect on permeate flux decline and TOC rejection. This is illustrated by the data displayed in Figs. 18, 19 and 20 for the runs of set III carried out at the highest HA feed concentration of 50 ppm are. The permeate flux data in Fig. 18 show that all runs exhibited a substantially equal decline of about 25%, regardless of the initial permeate level. The data of of the fractional flux decline plotted in Fig. 19 support the conclusion that the initial permeate level did not exert a significant effect on the flux decline. Fig. 20 clearly shows that the initial permeate flux level did not exert an effect on the TOC rejection.

Table 4
Effect of the initial flux level on flux decline and TOC rejection

Set	HA conc. (ppm)	Velocity (cm/s)	Temp. (°C)	Run No.	Initial flux (lmh)	Flux reduction in 300 min	TOC rejection
I	5	86.3	24	U17	73	~10%	50±20%.
				U16	83	~25%	50±20%.
II	20	86.3	28	U20	82	35%	80%
				U35	158	35%	80%
III	50	86.3	24	U18	66	~25%	85%
				U14	73	~25%	85%
				U11	92	~25%	85%

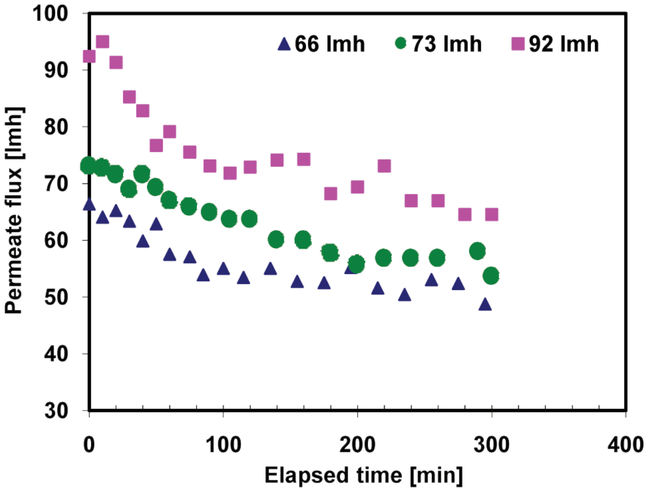

Fig. 18. Effect of the initial permeate flux on the permeate flux decline with time (set III).

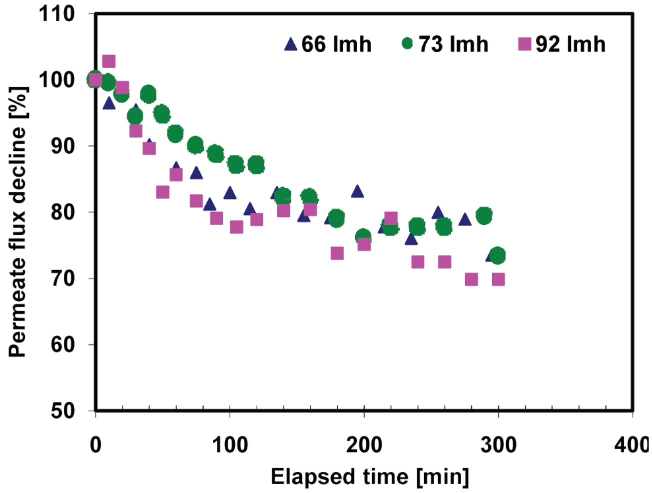

Fig. 19. Effect of the initial permeate flux on the fractional flux decline with time (set III).

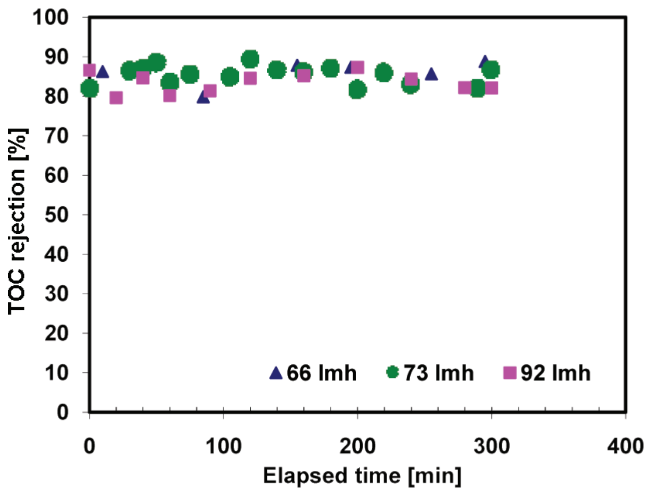

Fig. 20. Effect of the initial permeate flux on the TOC rejection (set III).

5.5. Macro analysis of permeate TOC concentrations

One of the main advantages ascribed to UF pre-filtration is that it yields a constant permeate quality, regardless of an increase in feed concentration, as for instance, might be the case in stormy weather conditions. Macro analysis of the UF results supports this observation. Fig. 21 displays the mean permeate TOC level as a function of the HA feed concentration fo all tests performed with the PVDF 100 kDa membrane. The confidence intervals of the data points, analyzed by a t-test at a 90% probability level, reflect TOC changes arising from variation of operating conditions in the various tests. The confidence intervals are seen to be relatively narrow. The overall result is that the PVDF 100 kDa membrane was able to provide a permeate with a practically constant TOC concentration of 1.5–3.5 ppm, regardless of the HA feed concentration (2–50 ppm) and other changes in the operating conditions.

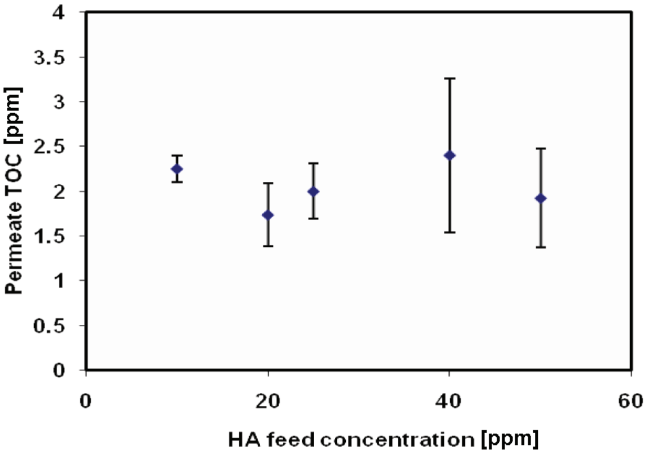

Fig. 21. Mean permeate TOC vs. HA feed concentration (PVDF 100 kDa membrane).

6. Concluding remarks

The main contributions of this study are in two directions. The first contribution lies in the novel approach for rational characterization of the separation "cut" of a filter medium by TOC measurements coupled with particle size distributions.

The second contribution lies in deep bed filtration data demonstrating that a granular medium is capable of providing a filtrate of practically constant quality over a rather wide range of operating conditions. A constant product quality is usually invoked as a conspicuous advantage of the UF system. It appears that deep-bed filtration can also provide filtrate of constant quality over a rather extensive range of conditions.

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References

[1] L. Henthorne, Economic evaluation of membrane and conventional SWRO pretreatment — results from pilot study, Proc. AWWA Conference on Membrane Technology, Phoenix, AZ, March 2005, pp. 1308–1321.

[2] N. Voutchkov, Seawater Pretreatment, Water Treatment Academy, TechnoBiz Communications Co., 2010, 174 pp.

[3] A. Mosset, V. Bonnelye, M. Petry and M.A. Sanz, The sensitivity of SDI analysis: from RO feed water to raw water, Desalination, 222 (2008) 17–23.

[4] M. Ando, S. Ishiara, H. Iwahori and N. Tada, Peculiar or unexpected behaviour of silt density index of pretreated water for desalination, IDA BAH 03-071.

[5] M.T. Valade, W.C. Becker and J.K. Edzwald, Practical paper — Treatment selection guidelines for particle and NOM removal, J. Wat. Supply Res. Technol. — AQUA, 58 (2009) 424–432.

[6] I. Sutzkover-Gutman, Performance improvement of polymeric membranes, PhD thesis, Technion — Israel Institute of Technology, Haifa, April 2010.

[7] J.G. Jacangelo, J. DeMarco, D.M Owen and S.J. Randtke, Selected processes for removing NOM: an overview, J. AWWA, 87 (1995) 64–77.

[8] I. Sutzkover-Gutman, D. Hasson and R. Semiat, Humic substances fouling in ultrafiltration processes, Desalination, 261 (2010) 218–231.

[9] W. Yuan and A. Zydney, Humic acid fouling during ultrafiltration, Environ. Sci. Technol., 34 (2000) 5043–5050.

[10] Z. Domany, I. Galambos, G. Vatai and E. Bekássy-Molnár, Humic substances removal from drinking water by membrane filtration, Desalination, 145 (2002) 333–337.

[11] I. Galambos, G. Vatai and E. Bekássy-Molnár, Membrane screening for humic substances removal, Desalination, 162 (2004) 111–116.

[12] A.R. Costa and M.N. de Pinho, Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions, J. Membr. Sci., 255 (2005) 49–56.

[13] H.A. Mousa, Investigation of UF membranes fouling by humic acid, Desalination, 271 (2007) 38–51.

[14] J. Lowe and Md.M. Hossain, Application of ultrafiltration membranes for removal of humic acid from drinking water, Desalination, 218 (2008) 343–354.