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Wastewater treatment of paper industry by microfiltration and ultrafiltration

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ABSTRACT

In the production of paper, an effluent with high organic load is generated, and conventional treatments alone are not able to remove all this load. Due to this problem, this research aimed to evaluate and compare the application of microfiltration and ultrafiltration filter membranes in the treatment of white water from paper industry. Trials in a pilot unit for microfiltration and ultrafiltration were performed for a later comparative analysis of apparent color removal efficiencies, COD, and turbidity of the effluent, and the permeate flow in the different filtration technologies was also evaluated. The membranes used have the same fiber length (26 cm), fiber diameter (25 mm) and filtration area (0.09 m²); however, the average pore diameter is different: 0.4 µm in microfiltration membranes and 50 kDa in ultrafiltration membranes. The results obtained indicated that microfiltration and ultrafiltration present high efficiency in reducing the parameters studied: 97% apparent color removal for both technologies, 78.26% COD for MF, and 82.75% for UF and 99% turbidity for both. The main difference between these two filtration methods is in the permeate flow, which is significantly higher in MF, indicating that with this technology it is possible to treat a higher effluent flow without losing efficiency.

Index terms: apparent color, COD, effluents, papermaking,turbidity.

Tratamento de efluentes da indústria de papel por microfiltração e ultrafiltração

Ideias centrais

- Similaridade entre as características das membranas filtrantes sintéticas e naturais.
- Microfiltração (MF) e ultrafiltração (UF) filtram sem provocar alterações bioquímicas.
- Tratamento de efluentes industriais é necessário para o consumo sustentável de água.
- MF e UF como tratamento alternativo para efluentes de indústrias de papel.

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RESUMO

Na produção de papel é gerado um efluente com elevada carga orgânica, e apenas os tratamentos convencionais não são capazes de remover toda essa carga. Em face desse problema, esta pesquisa teve como objetivo avaliar e comparar a aplicação de membranas filtrantes de microfiltração e ultrafiltração no tratamento de água branca da indústria do papel. Foram realizados ensaios numa unidade piloto de microfiltração e ultrafiltração para uma análise comparativa posterior das eficiências aparentes de remoção de cor, DQO e turbidez do efluente, e o fluxo de permeado nas diferentes tecnologias de filtração também foi avaliado. As membranas utilizadas têm o mesmo comprimento de fibra (26 cm), diâmetro de fibra (25 mm) e área de filtração (0,09 m²); contudo, o diâmetro médio dos poros é diferente: 0,4 µm em membranas de microfiltração e 50 kDa em membranas de ultrafiltração. Os resultados obtidos indicaram que a microfiltração e a ultrafiltração apresentam alta eficiência na redução dos parâmetros estudados: 97% de remoção de cor aparente para ambas as tecnologias, 78,26% de DQO para MF, e 82,75% para UF e 99% de turbidez para ambas. A principal diferença entre esses dois métodos de filtração está no fluxo de permeado, que é significativamente maior em MF, indicando que, com essa tecnologia, é possível tratar um maior fluxo de efluentes sem perder eficiência.

Termos para indexação: cor aparente, DQO, efluentes, fabricação de papel, turbidez.

INTRODUCTION

To reduce the amount and improve the quality of industrial effluents, numerous methods have been tested for the development of cheaper and more effective technologies (Sharma et al., 2020), such as photocatalysis, coagulation and flocculation, flotation, membrane filtration and others (Barakat, 2011; Fu & Wang, 2011). Among these, membrane separation has gained prominence, as it enables the generation of water reusable in industrial processes (Galvão & Gomes, 2015; Kamali et al., 2019).

In this system, synthetic membranes are used, which are assimilated to the selectivity characteristics of natural membranes, thus obtaining a final effluent of better quality. These selective barriers limit, partially or totally, the permeance of unwanted particles in the membrane, without chemical or biological transformation occurring during filtration, through the application of a hydraulic pressure gradient or electric field to allow separation (Hubbe et al., 2016). Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED) are the most used techniques.The difference between them lies in the retention capacity, in the way they separate the polluting particles, and in the type and intensity of the driving force that is applied (Jordão & Pessôa, 2017; Calijuri & Cunha, 2019).

The membrane modules can be operated in two ways: tangential and frontal. In tangential filtration, the flow occurs in a crossflow way, the feeding solution flows parallel to the membrane surface, while the permeate passes transversally to it (Baker, 2012; Ismail et al., 2018). On the other hand, in frontal filtration, the feeding is performed perpendicular to the membrane surface (dead end), so that the suspended particles accumulate on this surface (Habert et al., 2006). The transverse mode has many advantages in controlling concentration polarization and clogging, thus reducing transport resistance, and keeping permeate flow at high value for long operational periods (Davis, 1992; Mulder, 1996).

To make the operation of membrane systems feasible, it must be ensured that the operating pressure determined for filtration to occur is as low as possible over long periods, without loss of efficiency and without a high decline in permeate flow occurring. Thus, compaction and reversible or irreversible accumulation of material on the surface of the membranes are relevant factors, with a tendency for the feed water to block the membranes, one of the most important design parameters in the creation of the filtration system (Calijuri & Cunha, 2019).

The paper mill is a great consumer of water andit can be stated that there is a proportional relationship between the consumption of fresh water and the generation of effluents during the production process (Man et al., 2018). This way, the treatment of effluents is necessary to satisfy the basic demand for water for human consumption and for industrial use (Voulvoulis, 2018).

The main effluent from the paper millis white water – such term is used to define the aqueous solution present in the paper machine system, which is drained during the sheet forming process.

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The components of white water can be considered inorganic, organic, and biological. They can also be classified as dissolved or suspended, contributing to about 700 to 1,400 mg L^{-1} of biochemical oxygen demand (BOD) and 1,900 to 3,200 mg L^{-1} of chemical oxygen demand (COD), which should be removed in the following industry effluent treatment processes (Lacorte et al., 2003; Hubbe, 2007).

For the oxidation of the residual organic matter contained in the effluent to occur and in order to be forwarded to the final treatment stage, high consumption of dissolved oxygen is required. To reduce the biochemical and chemicaldemand for oxygen, this work aimed to evaluate the technical feasibility of removing residual components from white water by the processes of microfiltration (MF) and ultrafiltration (UF) by membranes.

MATERIAL AND METHODS

Wastewater collection

The white water used in this research was collected in the output channel of a paper machine, in an industry in the countryside of the state of Paraná, Brazil. The papers produced at the time of collection were “white kraft” type for packaging, monolucid and offset. The paper machine has a fiber recovery system by disc filters, to recover fibers and part of the mineral load; however, the fiber content that reaches the Effluent Treatment Station (ETS) is still high.

The average flow of the white-water effluent is approximately 50 m^3 h^{-1} and the concentration of suspended solids in the effluent is 350 to 500 mg. L^{-1}. The effluent collected was packed in gallons of polyethylene with a capacity of 25L according to ABNT NBR 9898 (ABNT, 1987) and transported to the environmental sanitation and water quality laboratory of the environmental engineering department of the Universidade Estadual do Centro-Oeste, in the Irati campus, state of Paraná for further characterization and testing at the MF and UF pilot plant.

Physicochemical characterization of wastewater

The parameters for the assessment of wastewater were apparent color, chemical oxygen demand (COD), pH, sedimentable solids, total suspended solids, total solids, and turbidity. Table 1 shows the values of these parameters of the wastewater at the time of collection.

Table 1. Physicochemical parameters of the wastewater.

Parameter	Unfiltered wastewater	Method[1]
Apparent color, uC	948	2120C
COD, mg L^{-1}	810.42	5220D
pH	7.19	4500B
Sedimentable solids, mg L^{-1}	80	2540F
Total suspended solids, mg L^{-1}	27	2540B
Total solids, mg L^{-1}	278	2540B
Turbidity, NTU	226	2030B

[1]Determined according to Eaton et al. (2005).

Microfiltration (MF) and Ultrafiltration (UF)(T2)

Microfiltration and ultrafiltration were performed in a membrane bench pilot unit (PAM MembranasSeletivas Ltda., Rio de Janeiro, Brazil) based on tangential filtration performing from the outside to the inside of the hollow membrane fibers, with diaphragm pump and working pressure of up to 4 bar, using 10 liters of wastewater in total recirculation system (Figure 1). Table 2 describes the characteristics of the membranes used.

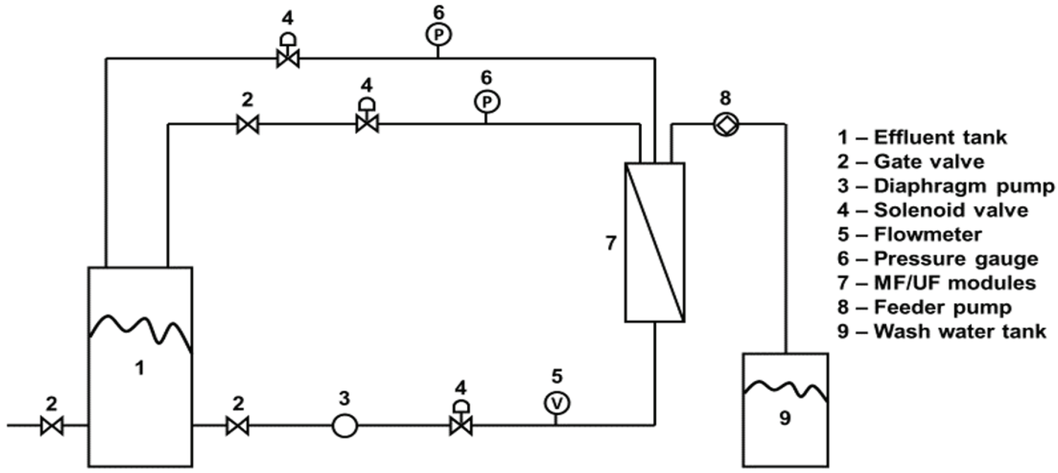

Figure 1. Layout of the membrane bench pilot unit.

Source: adapted from Neves et al. (2017).

Table 2. Microfiltration and ultrafiltration membrane features

Features	Microfiltration (MF)	Ultrafiltration (UF)
Material	Polyetherimide	Polyether(sulfone)
Fiber length, cm	26	26
Fiber diameter, mm	25	25
Average pore size	0.4 µm	50 kDa(1)
Filtration area, m²	0.09	0.09

(1) Unit corresponding to cutting molar mass where 90% of the solutes with equal molar mass are retained in the membrane.

In this research the adopted working pressure was 0.25 bar, defined by the critical flow, feed flow of 144 L min^{-1} in a total test duration of 120 minutes. During the filtrations the permeate flow was continuously measured at regular intervals of 10 minutes and the permeate sample was collected every 30 minutes for subsequent physical-chemical tests. During the test period, backwashing was performed at 10-minute intervals lasting 30 seconds to remove solids accumulated on the membrane surface to minimize fouling formation.

Permeate flow and efficiency

The permeate flow was measured by means of a precision chronometer and a 10 mL test tube, performing the conversion of the flow unit.

To evaluate the efficiency of the treatment, the following features were evaluated: the reduction in the values of turbidity, truecolor, and COD parameters during the two hours of analysis every 10 minutes. The evaluation of efficiency was determined by Equation 1.

$$E_x(\%) = \left[\frac{(CO - CI)}{CO}\right] \cdot 100 \qquad \text{(Equation1)}$$

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where E: treatment efficiency in percentage; X: turbidity, realcolor, or COD; CO: parameter value in unfiltered wastewater; CI: parameter value in filtered wastewater.

Statistical analysis

All the analysis of this research was performed in three repetitions.

Evaluation and comparison of MF and UF membrane performance in the treatment of the effluent under study were performed. The variables used during the operation test were analyzed and compared using two hierarchical factors where the main factors were the membranes (MF and UF), and the operation time (30, 60, 90 and 120 minutes) factor was subjected to the membrane type factor.

The data were previously checked for residue gaussianity and variance homogeneity by Kolmogorov-Smirnov and Bartlett tests, respectively. The difference between the means was measured by Tukey's test. The significance level for all tests was 5%.The statistical analyses were performed using the Statistica® software, version 10.

RESULTS AND DISCUSSION

Permeate flow

One of the most relevant points in the membrane separation process is the ability to maintain permeate flow without significant reduction. Due to the larger pore size, the MF membrane has less resistance to bloom (Cheryan, 1998), and this characteristic has caused significant statistical differences in permeate flow (Figure 1). The MF permeate flow is higher than UF, with an average value of 62.48 L h^{-1} m^{-2} for MF and 12.56 L h^{-1} m^{-2} for UF.

The permeate flow showed a slight decline until the end of the experiment (Figure 2), and this occurs due to the accumulation of particles larger than the pores on the surface of the membrane, resulting in a reduction in the useful filtration area (Chang et al., 2016). Even so, it is possible to operate MF and UF technologies without increasing the transmembrane pressure, maintaining a regular flow in the treatment of paper making wastewater.

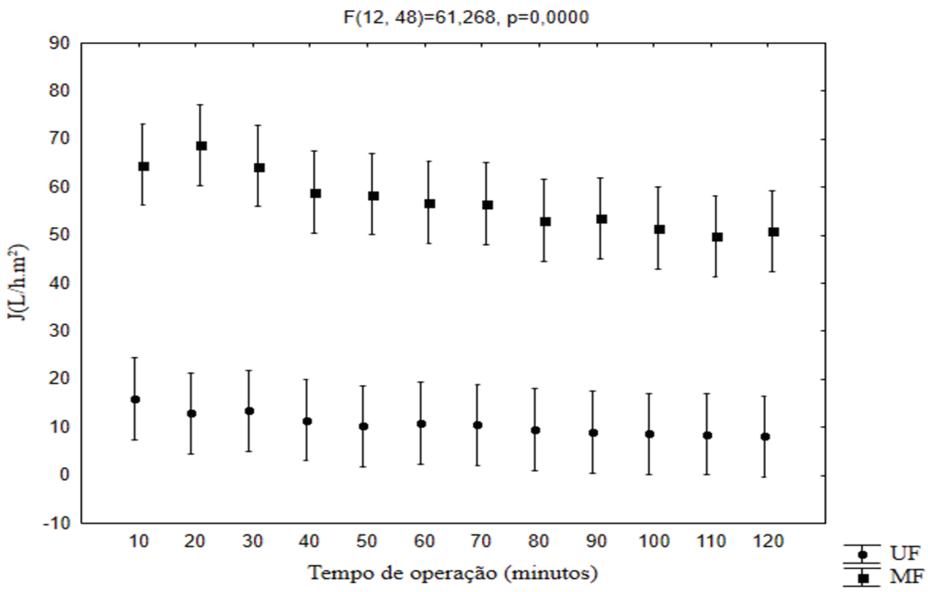

Figure 2. Permeate flow profile in relation to the operating time of MF and UF treatments.

Efficiency

The MF and UF membranes were extremely effective in reducing the turbidity of the samples and were able to remove 99% of the turbidity at the end of the treatment. This occurred due to the average pore size of the membranes, which allowed the retention of the suspended material contained in the effluent, being responsible for the turbidity. In this research the type of membrane influenced statistically the turbidity of the effluent (Figure 3), with absolute values of 1.17 µT and 2.05 µT for MF and UF, respectively. On the other hand, time did not influence this characteristic.

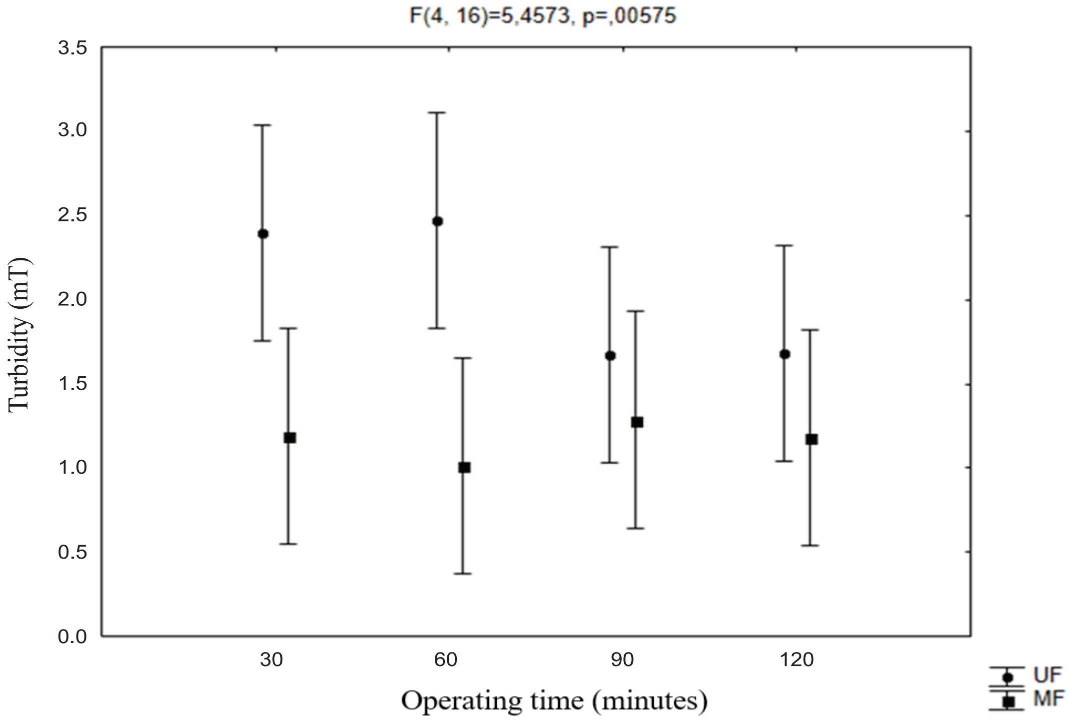

Figure 3. Average turbidity removal values in relation to the operating time in MF and UF technologies.

Turbidity is a physical property of fluids that translates into reduced transparency due to the presence of suspended materials that interfere with the passage of light through the fluid. In the treatment of paper industry effluents, MF and UF tend to remove almost all suspended solids, as these solids have particle sizes greater than 0.5 µm (Robusti et al., 2014). This makes the capacity of reduction of the turbidity of the wastewater from papermaking with MF and UF close to 100% (Sakurai et al., 2016).

Color that is free of turbidity after going through the membrane filtration process is called true color (Manual…, 2014). It can be considered a highly interfering factor in the photosynthetic process that occurs naturally in receiving water body, causing the alteration in the aquatic biota, in a more intense way, in the surroundings of effluent discharge by industries (Bertazzoli & Pelegrini, 2002).

The membranes obtained the removal efficiency of 97% of the colloidal material in suspension, which interferes with the measurement and determination of the true colors of the effluent without statistical difference between them and without statistical effect of time, so the color removals that occurred in the first minutes of filtration were satisfactory for both membranes tested, where 29.3 µC was measured in MF permeate and 35.7 µC in UF in absolute values (Figure 4).

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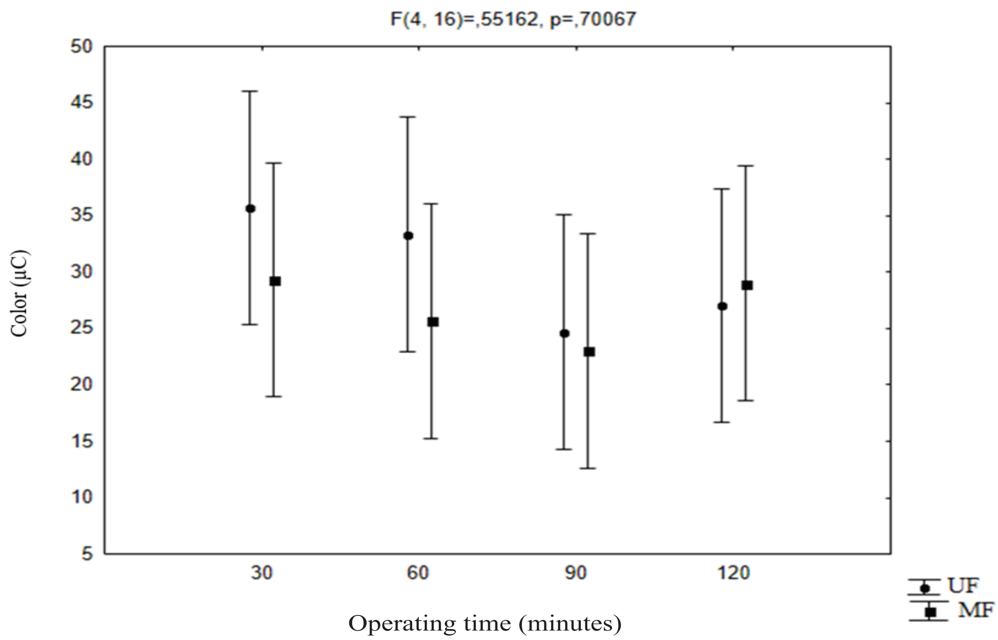

Figure 4. Apparent color from treated effluent analysis in relation to the operating time in MF and UF technologies.

The chemical oxygen demand (COD) corresponds to the amount of specific oxidizer that is consumed by the samples under controlled conditions. The amount of oxidizer that is consumed will be its oxygen equivalence. For this variable there was statistical difference between the membranes, reaching values of 78.26% and 82.75% of removal efficiency for MF and UF respectively– this means the membranes acted as a selective barrier, preventing the passage of particles with sizes larger than the pore size of the membranes. The mean values found were: for MF,176.19 mg L^{-1} for the permeate, and for UF, 139.80 mg L^{-1}. This is e xplained by the fact that UF membranes have smaller pores than the MF membranes, thus retaining a wider range of particles (Figure 4). These results are similar to those of Neves et al. (2017), who evaluated the efficiency of MF and UF in lignin-rich wastewater from pulp and paper mill.

Figure 5 displays the treated COD of organic matter from MF and UF processes over time of operation.

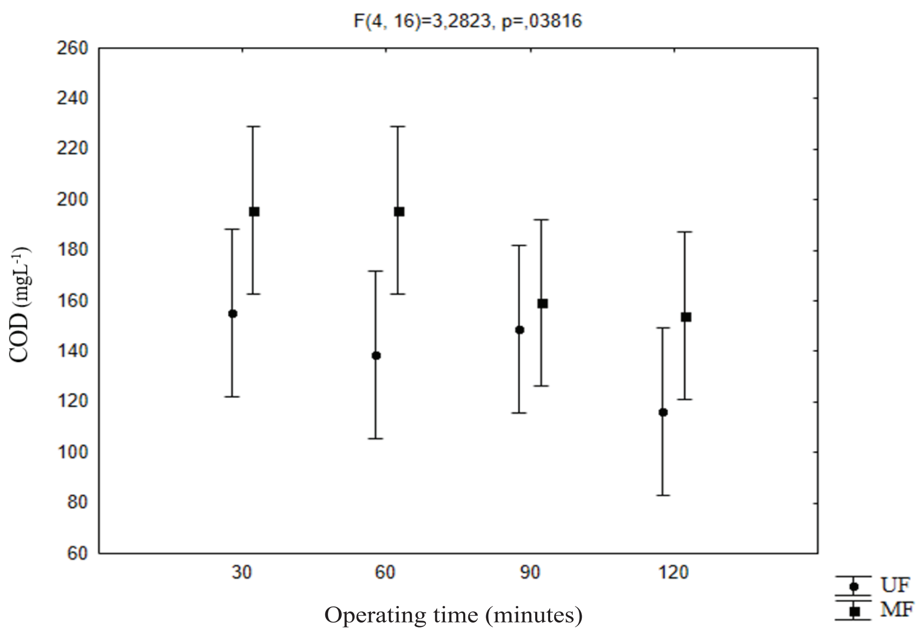

Figure 5. Treated COD of organic matter from MF and UF processes over time of operation.

This effluent has a high organic matter content in the dissolved phase that can remain after treatment. The ultrafiltration membrane has better performance in COD reduction, due to the smaller size of its pores, thus making it possible to retain more contaminating particles.

There is no statistical difference between the different COD measurement times, indicating that the shorter time is already sufficient to obtain the best result.

CONCLUSION

MF and UF presented satisfactory results due to the high efficiency in reducing the studied parameters. However, the MF membrane provided higher permeate flow in relation to UF. This factor indicates that a higher volume of white water can be treated with the MF membrane in a higher flow.

Neither the type of membrane nor the filtration time influenced the true color, but MF obtained the best reduction in turbidity, while UF obtained the best reduction in COD. These last two characteristics were not influenced by time either.

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