



## Removal of NOM from concentrates produced by an ultrafiltration system treating drinking water

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### Abstract

The decline of flux caused by Natural Organic Matter (NOM) is a major restriction to the wide utilization of membrane systems. A UF pilot plant (UFPP) treating water from the Guarapiranga Reservoir in Metropolitan São Paulo has shown concentrates with high NOM concentrations. In order to assess possibilities of NOM removal a Physical Chemistry (FC) process was set producing clarified water with characteristics similar to those of the Guarapiranga raw water, allowing to its recycling to the pilot plant feed tank. Removals of color, UV<sub>254 nm</sub> and COT achieved are in the order of 90%, 70% and 60%, respectively.

*Keywords:* Ultrafiltration; concentrate; NOM removal; clarification; recycling.

### 1. Introduction

Due to the increasing restrictions on regulations for drinking water quality membrane systems have shown to be the technology of choice to provide safe water. Low pressure membranes such as microfiltration (MF) and ultrafiltration (UF) substitute conventional treatment systems, allowing for the supply of high quality waters at competitive costs [1-2].

The UF system treating water from Guarapiranga Reservoir produced concentrate with high concentrations of organic matter [3], which may cause disposal problems, organic fouling and the decline of permeate flux. Several studies have shown that the major drawback of membrane systems are the drop of production caused by fouling as well as the final disposal of concentrates. Natural Organic Matter (NOM) is recognized as the more important cause of both restraints. [1, 4-6]. Moreover, the NOM is main limitation to the achievement of adequate recovery ratio in membrane drinking water treatment (70% to 95%). Spiral wound membranes for example, operating at fluxes from 25 to 30 L/h/m<sup>2</sup> can have a capacity drop of more than 75% in 2000 h of operation [6]. Mierzwa et al [7] have shown that the presence of organic matter requires chemical cleaning every week and when organic matter is removed by oxidation, chemical cleaning is needed once a month. The consequences of fouling in membrane systems leads to increasing energy costs, flux decline, increase of transmembrane pressure and membrane lost, in more critical cases. On the other hand the presence of NOM may change the water quality of catchments, affecting consequently the operation and maintenance procedures of water treatment plants [8-9]. Moreover, can be also harming to the health of consumers since the presence of NOM may lead to formation of disinfection by-products. [9-12].

This study aims at the treatment of concentrates produced through an UF pilot plant, in order to minimize discharge effects on the environment, to reduce impacts to the membrane

system, as well as to the increasing permeate production by recycling of the treated concentrate in UFPP.

## 2. Materials and Methods

The tests were carried out with the concentrate from an ultrafiltration pilot plant (UFPP) installed next to the Guarapiranga Reservoir. Continuous operation begun on August 2007 aiming at performance evaluation for drinking water treatment.

### 2.1. Ultrafiltration Pilot Plant - UFPP

The UFPP includes a spiral wound ultrafiltration membrane from GE-Water model PW-4040F, with a molecular weight cutoff of 10,000 Daltons. It operates continuously but with intermittent discharge of concentrates (Figure 1). Chemical cleaning was carried out once a month, using sodium chloride and detergent as cleaning agents and peracetic acid for sanitization. Figure 2 shows the normalized permeate flow (25 °C) of the UFPP system. Table 1 shows the water quality parameters of raw water and permeate, and Table 2 shows the final concentrate quality.

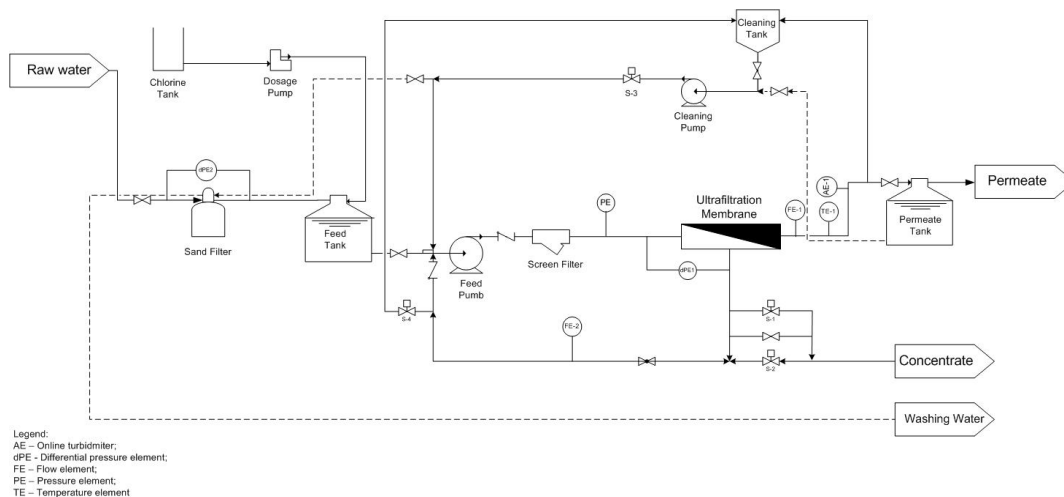


Fig. 1. Flowchart of the ultrafiltration pilot plant

### 2.2. Bench scale clarification

Tests for initial clarification evaluation were performed on a bench scale basis using a Jar-Test unit (Milan Equipamentos Científicos Ltda, model JT-203/06). Chemicals utilized were ferric chloride as coagulant, iron dosage ranging from 2.1 to 16.6 mg Fe<sup>3+</sup>.L<sup>-1</sup>, pH adjusted with hydrochloridric acid or sodium hydroxide, in the range of 4.5 to 7.0 (all with analytical grades from Labsynth Produtos para Laboratório Ltda). The data obtained allow for the preparation of a coagulation diagram. Clarification efficiency was evaluated based on color and UV light absorption reduction, using a color meter from Policontrol, Aqua Color model, and an UV/Visible spectrophotometer from Micronal SA, B382 model. Jar-test operational conditions used for obtaining coagulation diagram were:

- Rapid mixing: velocity gradient: 120 s<sup>-1</sup>, time: 2 minutes;
- Slow mixing: velocity gradient: 40 s<sup>-1</sup>, time: 20 minutes;

- Sedimentation time: 20 minutes.

Samples for analysis were drawn 7.5 cm from the surface of each jar, resulting in a settling velocity of  $6.25 \times 10^{-3} \text{ cm.s}^{-1}$ .

### 2.3. Concentrate Clarification Pilot Unit – CCPU

The CCPU used for clarification was designed to treat the concentrate flow from the UFPP, of about  $20 \text{ L.h}^{-1}$ . This pilot unit is made of an accumulation tank, feeding system and dosing pumps, a flocculation reactor and a settling tank, as shown in Figure 2. The accumulation tank has an inner diameter of 0.30 m and 1.00 m of depth. The flocculation reactor with a square cross section is 0.174 m wide and 0.168 m high, and the settling tank has an inner diameter of .30 m, and 1.00 cm of depth.

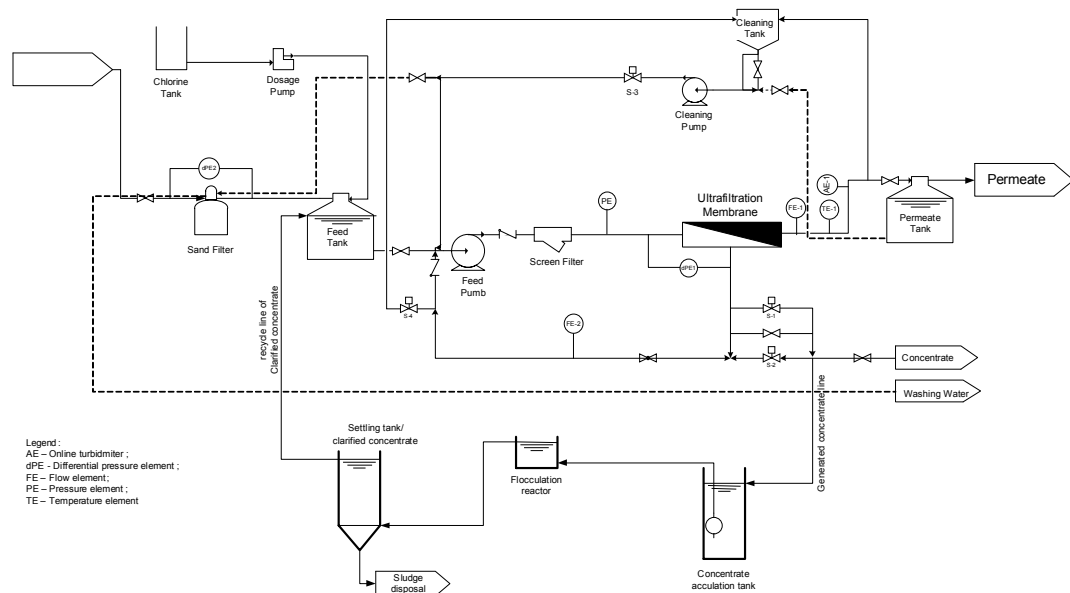


Fig. 2. Flowchart of the ultrafiltration pilot plant with the clarification pilot unit

From January.09.2009 to January.30.2009, the CPU was operated in batch mode, and from February.03.2009 to February,09.2009 under continuous flow. During the batch operation, samples were collected once a day, and during continuous operation every hour, during a period of 8 hours. All samples were analyzed for pH, (Quimis Aparelhos Científicos Ltda, model Q-400MT), for turbidity, (Policontrol, T100 ) color,(Policontrol, AcquaColor)  $UV_{254}$  absorption,(Micronal, SW) and TOC, (Shimadzu, TOC-VCPH). Ferric chloride dosing control was made using the pH-meter, with the probe submerged in the flocculation tank. This procedure was adopted since there were no need for pH adjustment.

### 2.4. UFPP performance treating raw water plus recycled clarified concentrate.

The clarified concentrate was recycled to the UFPP feed tank. The UFPP performance was evaluated with basis on data from the permeate flow and from turbidity measurements, registered by a data logger (Novus Produtos Eletrônicos Ltda, FieldLogger model).

A comparison between the quality of the clarified concentrate and of the reservoir raw water was made in order to evaluate the environmental effect.



### 3. Results

#### 3.1. Raw water quality

The quality of raw water from the Guarapiranga reservoir, of the concentrate and of the permeate have been monitored since 2007 by a before research. The related data are shown in Tables 1 and 2.

Table 1 - Raw water and permeate quality parameters of UFPP

Quality Parameter		Number of samples	Results			Standard Deviation
			Average	Minimum	Maximum	
Turbidity (UNT)	permeate	15	0.24	0.06	0.78	0.23
	raw	15	4.26	1.1	11.23	3.27
Color (color unit)	permeate	12	4.57	2	7.67	1.94
	raw	12	73.19	25.33	190	45.71
UV light absorption (cm-1)	permeate	16	0.049	0.02	0.066	0.013
	raw	16	0.112	0.063	0.307	0.073
TOC (mg.L-1 as C)	permeate	15	3.27	1.9	4.53	0.693
	raw	15	5.87	3.48	14.63	3.333
pH (unit)	permeate	16	7.481	7.026	8.019	0.254
	raw	16	8	7.39	11.49	1.014
Total Coliform (MPN/100mL)	permeate	8	0.375	0	2	0.744
	raw	8	931.025	63	2419.6	1067.949
E. Coli (MPN/100mL)	permeate	9	0.0	0.0	0.0	0.0
	raw	9	46.28	7.4	155.3	53.73
Conductivity (µS.cm-1)	permeate	15	171.61	139.57	200	17.589
	raw	15	262.08	136.07	687	281.782

Table 2 - Concentrate samples characterization results

Quality Parameter	Number of samples	Results			Standard Deviation
		Average	Minimum	Maximum	
Turbidity (NTU)	15	15.38	2.57	45.8	14.61
Color (color unit)	12	164.05	103.3	251.4	46.28
UV light absorption (cm-1)	16	0.204	0.085	0.325	0.077
TOC (mg.L-1 as C)	15	12.38	4.1	24.6	5.067
pH	16	7.52	7.39	7.87	0.134
Total Coliform (MPN/100ml)	8	269.9	14.1	906	316.609
E. Coli (MPN/100ml)	9	8.89	0	19.9	7.88
Conductivity (mS.cm-1)	15	196.77	103.3	229.33	30.796

### 3.1. Laboratory Tests

Figure 3 shows the coagulation diagram, indicating that the best condition for clarification of the concentrate, based on color removal is at a coagulant dosage above 12 mg  $\text{Fe}^{+3} \cdot \text{L}^{-1}$  and a pH lower than 5.5. Thus, for tests on the pilot scale unit, a pH ranging from 4.5 to 5, and a coagulant dosage above 12.4 mg  $\text{Fe}^{+3} \cdot \text{L}^{-1}$  were chosen. This result shows a similar behavior observed on the treatment of freshwater with a high concentration of NOM and low turbidity. It should be mentioned that the clarified samples were not filtered.

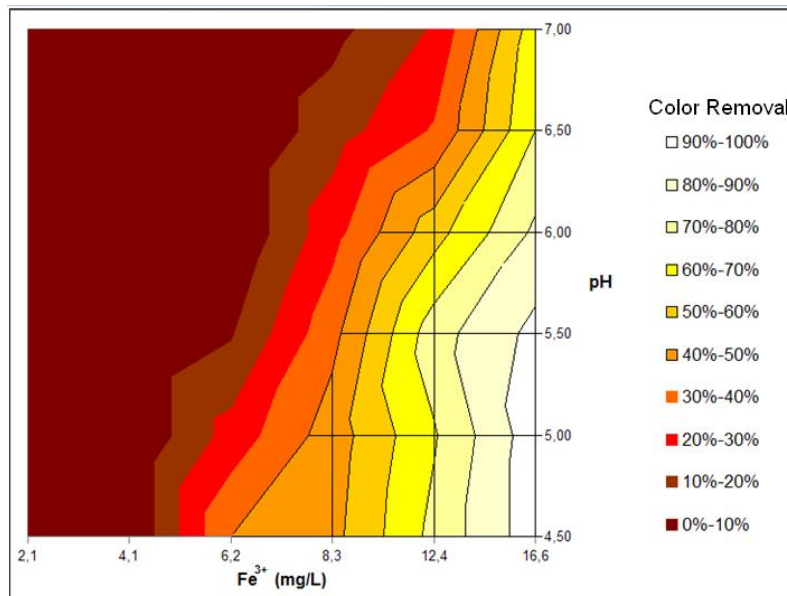


Figure 3 – Coagulation diagram of concentrate dosing Ferric Chloride

### 3.2. CCPU Performance

Tables 3 and 4 show the results of the clarification tests during batch and continuous operation. [8].

Table 3 - CCPU treated water sample characterization and efficiencies removal under batch operation

Parameter		Number of Samples	Results			Standard Deviation	Removal Efficiency
			Average	Minimum	Maximum		
Color (CU)	clarified	15	18.8	2.00	49.00	18.8	83%
	concentrate	15	113.5	91.0	244.4	52.06	
Turbidity (NTU)	clarified	15	0.68	0.02	2.19	0.82	90%
	concentrate	15	6.87	4.14	29.2	6.74	
UV254 ( $\text{cm}^{-1}$ )	clarified	16	0.102	0.057	0.214	0.046	71%
	concentrate	16	0.349	0.271	0.677	0.14	
TOC (mg/L)	clarified	16	5.36	3.15	9.89	1.87	62%
	concentrate	16	14.07	11.16	28.42	5.03	
pH	clarified	16	5.13	3.20	6.90	1.14	-x-
	concentrate	16	7.12	6.97	7.2	0.09	



Table 4 - CCPU treated water sample characterization and efficiencies removal under continuous operation

Parameter		Number of Samples	Results			Standard Deviation	Removal Efficiency
			Average	Minimum	Maximum		
Color (CU)	clarified	18	6.33	2.00	20	4.92	95%
	concentrate	18	117	64.0	204	63.8	
Turbidity (NTU)	clarified	18	0.131	0.02	0.53	0.17	99%
	concentrate	18	9.78	3.06	22.2	9.04	
UV254 (cm-1)	clarified	19	0.085	0.04	0.128	0.028	70%
	concentrate	19	0.281	0.17	0.428	0.11	
TOC (mg/L)	clarified	19	4.81	3.5	6.45	1.01	61%
	concentrate	19	12.50	11.0	13.67	1.15	
pH	clarified	19	4.97	4.32	5.71	0.49	-x-
	concentrate	19	6.68	6.48	6.87	0.16	

The results presented in Tables 3 and 4 show a significant removal of monitored parameters during the operation of the clarification system. By comparing the results from Table 3 and Table 4 with the ones from Table 1 for raw water, it can be concluded that the clarified concentrate recycling is feasible. Besides the clarification process efficiency, the influence of concentrate recycling on the UFPP performance was also evaluated comparing operational parameters stored on a data logger, before and after the recirculation of the concentrate. Figures 5 and 6 show the concentrate recycling influence on the UFPP performance, considering the variation of permeate flow and turbidity, respectively [8].

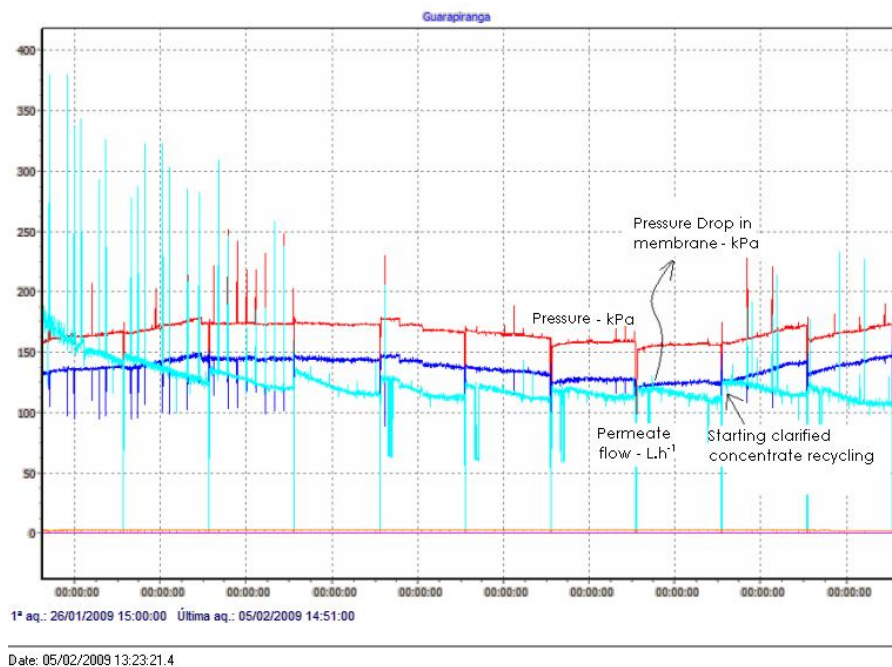


Fig. 5. Permeate flow from the UFPP before and after concentrate recycling.

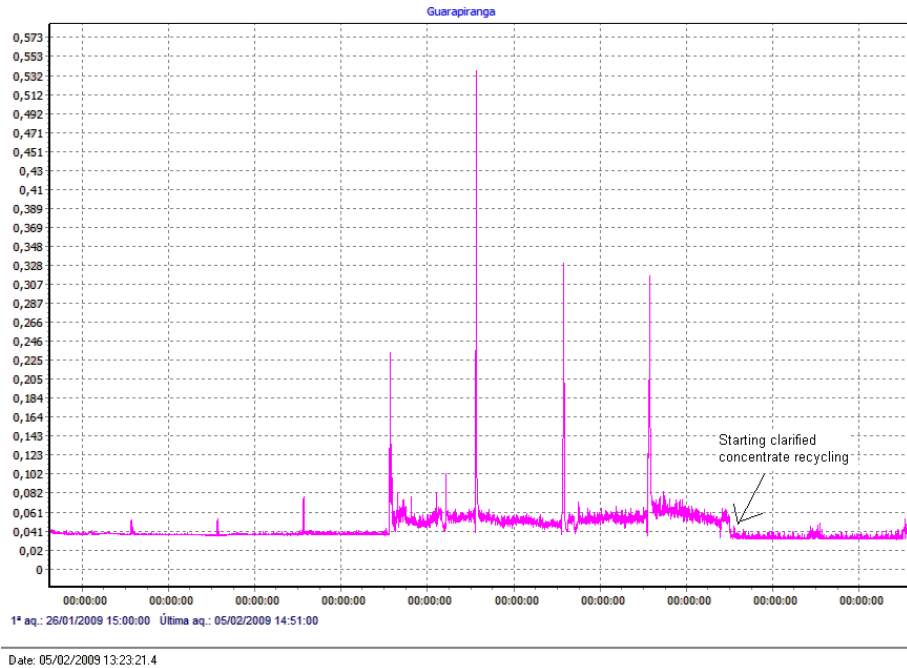


Fig. 6. Permeate turbidity from the UFPP before and after concentrate recycling

By analyzing Figures 4 and 5, it can be observed that both permeate production and turbidity remained at the same level after the concentrate recycling to the UFPP feed, demonstrating the feasibility of the clarification process for the treatment of concentrates from UF systems treating drinking waters.

#### 4. Conclusions

Based on the results produced by this study, it could be concluded that the clarification process is a very good option to improve membrane production and to reduce the environmental impact related to concentrate discharge.

Considering the main characteristics of the concentrate from the UFPP at the Guarapiranga Reservoir, a clarification process using ferric chloride as the coagulant and a pH in the range of 4.5 to 5 can efficiently be used to treat it, obtaining a clarified stream with a quality close to that of raw water.

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