

# The role of pH on the ultrafiltration for drinking water production in Algarve (Portugal)

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**Abstract** The effect of the pH on the ultrafiltration performance of natural surface waters with moderate NOM content was evaluated at a laboratory scale using a plate-and-frame polysulphone membrane of 47 kDa MWCO. The results at three different pH values (acid, neutral and basic) demonstrated the important role of the pH on the ultrafiltration (UF) performance controlling the membrane – fouling matter interactions. The higher fluxes and lower natural organic matter (NOM) rejections obtained, at basic pH when compared to acid pH, are explained in terms of the variation of membrane and NOM charge, due to electrostatic repulsion and adsorption effects.

**Keywords** Drinking water; pH adjustment; turbid water; ultrafiltration

## Introduction

The water supply system defined for the western part of Algarve, Portugal, is based on Alcantarilha Water Treatment Works (WTW), run by Águas do Algarve, SA, a holding of AdP, SGPE, SA. This WTW was designed to treat up to 3 m<sup>3</sup>/s (*c.a.* 1 million people, year 2020) of surface water by conventional treatment of preozonation, coagulation/flocculation/sedimentation, rapid sand filtration, pH adjustment and chlorination. It has three treatment lines in parallel, each one having 1 m<sup>3</sup>/s of capacity, to provide the seasonal drinking water demand (one line during winter and two or three lines during summer).

Considering that Alcantarilha's WTW must cope with seasonal changes in raw water quality and the continuous improvement of water quality must be ensured, technological upgrading studies based on membrane processes are being developed. This work presents the preliminary results of these studies: the evaluation of a pH adjustment of a turbid surface water to reduce membrane fouling and increase the ultrafiltration (UF) performance for drinking water production, without coagulant addition.

The effect of pH on UF performance is known. Stumm (1992) and Elimelech *et al.* (1994) suggest that pH affects both the surface charge of the membrane, and the configuration and solubility of the humic substances.

The surface charge of the membrane is dependent on the degree of ionization and, therefore, on the pH of the aqueous solution. At low pH, the membrane surface with amine functional groups can be positively charged, while at moderate to high pH, a membrane with carboxylic functional groups can be negatively charged. In the absence of ionizable functional groups, polymeric membrane surfaces can obtain a negative surface charge by anion adsorption present in solution (Elimelech *et al.*, 1994).

The humic substances, that include humic and fulvic acids, are refractory anionic polyelectrolytes of low to moderate molecular weight. They contain both aromatic and aliphatic components, mainly with carboxylic and phenolic functional groups (Stumm, 1992). As a result, humic substances are negatively charged in the pH range of natural waters. Similar to polyelectrolytes, humic substances are readily adsorbed onto solid surfaces in aqueous

solutions and markedly affect their electrokinetic charge (Elimelech *et al.*, 1994; Stumm, 1992). In addition, the pH also affects the humics' solubility, fulvic acids being soluble in acid alkaline conditions, whereas the humic acids are insoluble at low pH but soluble at high pH values (Schäfer *et al.*, 1998).

It seems that the dependency between the pH and the membrane charge conditioned the humic acids–membrane interactions. Below the membrane isoelectric point, where the membrane and the humic acid are oppositely charged, the adsorption of humic acids is favourable because of both electrostatic and hydrophobic interactions. Just above the isoelectric point, where the humic acids and the membrane are similarly charged, adsorption is dominated by hydrophobic interactions. At higher pH values, only minimal adsorption occurs because of the electrostatic repulsion between humic acids and the membrane surface and the increased hydrophilicity of humic acids (Childress and Elimelech, 1996).

Ruohomäki *et al.* (1998) evaluated the effect of pH on humic acid retention, using polyethersulphone membranes. They verified that fouling was higher at neutral pH than at acid or alkaline pH, which was attributed to the compact form of the humic acid at those pH values. Kabsch-Korbutowicz and Winnicki (1996) referred that the pH increase favours the fouling phenomena up to a certain value, above which there is a reduction in these phenomena.

## Experimental

### Water characterisation

Alcantarilha's WTW raw surface water has physical–chemical variations related to intense rainfall periods. After intense rainfall periods turbidity increases up to 20–40 NTU as well as total organic carbon (TOC) content (*c.a.* 6 mg C/l), while during dry periods turbidity is below 3 NTU and TOC varies from 1–3 mg C/l. The experiments were carried out from February–June 2000, during which the natural water was turbid (Table 1). Samples were collected before ozonation (raw water). The characteristics of these samples are shown in Table 1.

In all the samples, pH, turbidity, TOC and  $UV_{254nm}$  absorbance were measured. The pH was measured at 20°C with a Crison GLP22 pH meter. The turbidity was measured using a HACH 2100N turbidity meter of high resolution (0.001 NTU). TOC was measured using a Shimadzu 5050A (50 ppb–4,000 ppm) total organic carbon analyser. A Hitachi 2000 UV/VIS spectrophotometer was used to determine the  $UV_{254nm}$  absorbance. Water samples were not filtered before  $UV_{254nm}$  measurements. Therefore, it cannot be related directly with the humic substances, but also with turbidity particles.

The specific UV absorbance (SUVA), defined as  $DOC/UV_{254nm}$ , both parameters determined in filtered samples, values were 2.6–3.8 l/(m mgC). According to Edzwald and Van Benschoten (1990) these values are intermediate between natural organic matter largely composed of humic substances (SUVA values between 4 and 5, DOC is relatively hydrophobic) and non-humic materials (SUVA values less than 3, the organic matter is relatively hydrophilic).

**Table 1** Characteristics of the water samples

Date of collection	pH (at 20°C)	Turbidity (NTU)	$UV_{254nm}$ * (1/cm)	TOC (mg/l)
17 May 2000	7.65	34.50	0.32	3.54
29 May 2000	7.83	34.57	0.30	3.98
5 June 2000	7.60	33.70	0.29	3.48

\* No filtered samples

### UF experiments

UF experiments were performed with a GR40PP polysulphone membrane (336 cm<sup>2</sup>) from Danish Separation Systems (DSS) at 25°C, 2 bar and 1.3 m/s circulating velocity, using a plate-and-frame Lab-unit M10 from DSS. The plate-and-frame configuration simulates the hydrodynamics through the narrow channels of spiral-wound modules.

### Membrane characterisation

The membrane was first compacted permeating pure water (<1 μS/cm) at 4.5 bar for 3.5 hours. The membrane molecular weight cut-off (MWCO) was determined through the permeation of dilute aqueous solutions of reference solutes of increasing molecular weight, dextrans (DT 40,000, 70,000 and 110,000 Da, supplied by Pharmacia) and polyethylene-glycols (PEG 600, 3,000, 6,000, 10,000, 20,000 and 35,000 Da, supplied by Merck). The solute rejection,  $f$  ( $f = 1 - C_p/C_b$ , where  $C_b$  and  $C_p$  are the concentrations in the feed and in the permeate, respectively) was determined in terms of TOC. Feed samples were taken at the beginning and at the end of each experimental run, and the average was taken as the feed concentration,  $C_b$ .

The curve-fitting of  $\log(f/(1-f))$  versus solute molecular weight was intersected by 90% rejection line (Rosa and de Pinho, 1995) and yielded the MWCO of 47 kDa (Ribau Teixeira *et al.*, 2000).

The stabilisation time for each experimental run was 10 minutes. Between each run, membranes were washed with deionised water until pure water reached 90% of the initial value measured after compaction.

### Permeation of WTW water samples

These experiments consisted of concentration runs, simulating the industrial UF operation at different water recovery rates (WRR), defined as:

$$\text{WRR}(\%) = 100 \times \left( \frac{V_p}{V_b} \right) \quad (1)$$

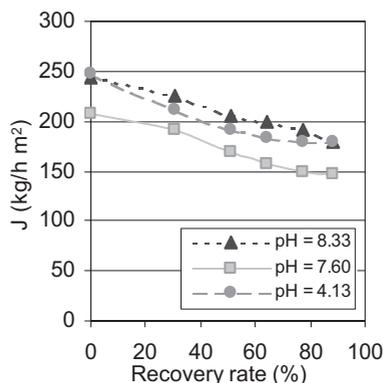
where  $V_p$  and  $V_b$  represent the permeate volume ( $l$ ) and the initial feed volume ( $l$ ), respectively.

In these runs, permeate does not recirculate to the feed reservoir until a stipulated permeate volume was obtained. At this time, permeate was recirculated to the feed reservoir during a 10 minute stabilisation period, after which a sample of the feed and a sample of the permeate were collected and the run followed to the next WRR. Experiments were performed at different pH values from 4–8. The pH was adjusted using H<sub>2</sub>SO<sub>4</sub> 0.02 M and NaOH 0.1 M (Merck p.a. reagent grade). Samples were analysed in terms of UV<sub>254nm</sub> absorbance and TOC. Between each run, membranes were washed with deionised water until pure water flux reached 90% of the initial value measured after compaction and pH reached the pH value of deionised water.

### Results and discussion

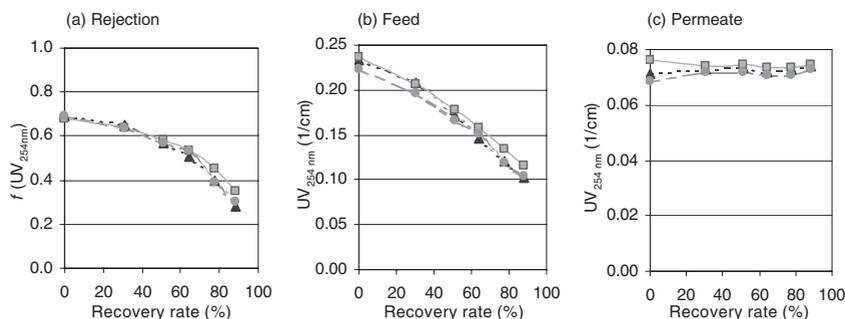
The results of flux are presented in Figure 1 and rejection, feed, and permeate quality data in terms of UV<sub>254nm</sub> absorbance and TOC are shown in Figure 2.

The experimental data obtained shows that, for the three pH values, the fluxes (Figure 1), and UV<sub>254nm</sub> and TOC rejections (Figure 2a, 2d) and UV<sub>254nm</sub> feed quality decreased (Figure 2b) with WRR, whereas permeate quality (Figure 2c, 2f) remained constant with WRR. Flux and rejections presented opposite behaviours, i.e. minimal fluxes and maximal rejections were obtained at neutral pH, while maximal fluxes and minimal rejections were verified at basic pH, especially for TOC measurements (Figure 1, Figure 2a and 2d).

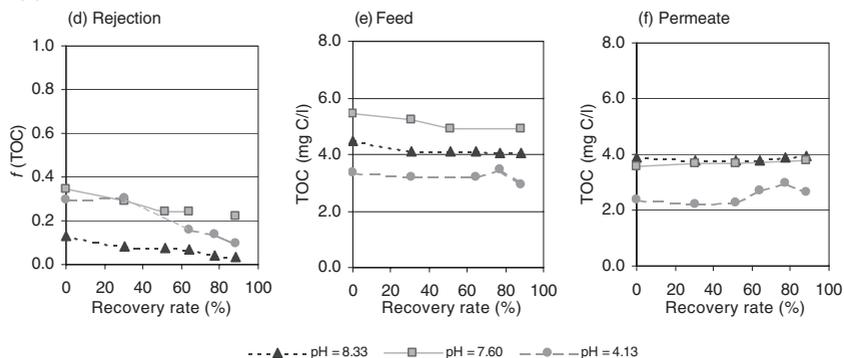


**Figure 1** Flux variation with water recovery rates pH values (25°C, 1.3 m/s, 2 bar)

### UV<sub>254nm</sub>



### TOC



**Figure 2** Rejection, feed, and permeate quality in terms of UV<sub>254nm</sub> (Figures 2a–c) and TOC (Figures 2d–f), with WRR, at different pH values (25°C, 1.3 m/s, 2 bar)

These results show the important role of the pH on the UF performance. The pH affects the membrane charge, the fouling matter charge and size and therefore the membrane-fouling matter interactions. At pH 4.13, the polysulphone membrane becomes less negatively charged and more carboxylic groups of NOM become protonated, reducing the charge of the humic macromolecules and therefore the repulsion among absorbing molecules. As a result, the electrostatic repulsion between the membrane and the humic substances decreases. In addition, protonation of the functional groups at low pH decreases the hydrodynamic radii of humic substances while increasing their hydrophobicity and their tendency to absorb (Jucker and Clark, 1994; Nazzal and Wiesner, 1994). Actually, NOM has a smaller macromolecular configuration at pH 4, due to the lower electrostatic repulsion between neighbouring functional groups, and thus it forms a dense fouling layer

(Hong and Elimelech, 1997). As a consequence, the flux decreases at acid pH when compared to basic pH (Figure 1) and the rejection increases (Figure 2).

A decrease in the feed concentration was observed for  $UV_{254nm}$  at the three pH values and for TOC at neutral pH (Figure 2). The decrease in the feed concentration of  $UV_{254nm}$  indicates that the fouling material adsorbs onto the membrane surface. Actually, this decrease is more pronounced than that observed for feed TOC concentration, whereas the  $UV_{254nm}$  rejections are always higher than those of TOC. This is due to the non-humic fraction (the water presents moderate values of SUVA), which is more hydrophilic and has lower molecular weight and, therefore, is less rejected and less adsorbed than the humic fraction and turbidity (expressed by  $UV_{254nm}$ ).

## Conclusion

The pH adjustment of turbid surface water with moderate NOM content significantly reduces membrane fouling and therefore increases the UF performance. The flux variation with the pH is dominated by the membrane–fouling matter interactions. For turbid waters, the electrostatic repulsion between membrane surface and NOM is reduced at pH 4.13 and protonation of the functional groups decreases the hydrodynamic radii of humic substances while increasing their hydrophobicity and their tendency to adsorb. Therefore, flux is lower at pH 4.13 than at pH 8.33.

The adjustment at basic pH is advantageous since the flux is higher and the water quality is the same for  $UV_{254nm}$ , slightly lower for TOC but higher in terms of final pH (non-aggressive water), when compared to acid pH of 4.13. As this study is concerned with water for human consumption, disinfection by-products of permeated water should be analysed.

## References

- Childress, A.E. and Elimelech, M. (1996). Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*, **119**, 253–268.
- Erdzward, J.K. and Van Benschoten, J.B. (1990). Aluminum coagulation of natural organic matter. In: *Chemical Water and Wastewater Treatment*. H.H. Hahn and R. Klute (Eds.), Springer-Verlag, Berlin, pp. 341–359.
- Elimelech, M., Chen, W.H. and Waypa, J.J. (1994). Measuring the zeta (electrokinetic) potential of reverse osmosis membranes by a streaming potential analyzer. *Desalination*, **95**, 269–286.
- Hong, S. and Elimelech, M. (1997). Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science*, **132**, 159–181.
- Jucker, C. and Clark, M.M. (1994). Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes. *Journal of Membrane Science*, **97**, 37–52.
- Kabsch-Korbutowicz, M. and Winnicki, T. (1996). Application of modified polysulfone membranes to treatment of water solutions containing humic substances and metal ions. *Desalination*, **105**, 41–49.
- Nazzal, F.F. and Wiesner, M.R. (1994). pH and ionic strength effects on the performance of ceramic membranes in water filtration. *Journal of Membrane Science*, **93**, 91–103.
- Ribau Teixeira, M., Lucas, H. and Rosa, M.J. (2000). Viabilidade da ultrafiltração para produção de água na ETA de Alcântarilha. *Recursos Hídricos*, **21**(3), 13–19.
- Rosa, M.J. and de Pinho, M.N. (1995). The role of ultrafiltration and nanofiltration on the minimisation of the environmental impact of bleached pulp effluents. *Journal of Membrane Science*, **102**, 155–161.
- Ruohomäki, K., Väisänen, P., Metsämuuronen, S., Kulovaara, M. and Nyström, M. (1998). Characterization and removal of humic substances in ultra- and nanofiltration. *Desalination*, **118**, 273–283.
- Schäfer, A.I., Fane, A.G. and Waite, T.D. (1998). Nanofiltration of natural organic matter: removal, fouling and the influence of multivalent ions. *Desalination*, **118**, 109–122.
- Stumm, W. (1992). *Chemistry of the Solid-Water Interface*. Wiley Interscience. New York.