Science of the Total Environment 621 (2018) 138–147

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Renewable energy powered membrane technology: Impact of pH and ionic strength on fluoride and natural organic matter removal

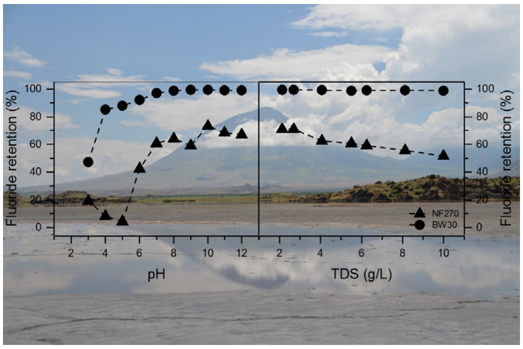
Isaac Owusu-Agyeman [a], Junjie Shen [b,c,1], Andrea Iris Schäfer [a,b,*]

[a] Membrane Technology Department, Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[b] Department of Water and Environmental Engineering, Nelson Mandela African Institute of Science and Technology, Arusha, Tanzania
[c] School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom

HIGHLIGHTS

- Tanzanian natural water with high F & NOM is treated by an autonomous NF/RO system.
- Low pH and high ionic strength increase permeate F due to size & charge effects.
- Water quality (pH & IS) affects 'loose' NF270 more than 'tight' BW30 membrane.
- NOM was retained <2 mg/L by both membranes with no significant effect of pH and ionic strength.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 July 2017
Received in revised form 3 November 2017
Accepted 9 November 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Fluoride
Natural organic matter
Nanofiltration
Reverse osmosis
pH
Ionic strength
Water quality

ABSTRACT

Real water pH and ionic strength vary greatly, which influences the performance of membrane processes such as nanofiltration (NF) and reverse osmosis (RO). Systematic variation of pH (3 — 12) and ionic strength (2–10 g/L as total dissolved solids (TDS)) was undertaken with a real Tanzanian water to investigate how water quality affects retention mechanisms of fluoride (F) and natural organic matter (NOM).

An autonomous solar powered NF/RO system driven by a solar array simulator was supplied with constant power from a generator. An open NF (NF270) and a brackish water RO (BW30) membrane were used. A surface water with a very high F (59.7 mg/L) and NOM (110 mgC/L) was used. Retention of F by NF270 was <20% at pH <6, increased to 40% at pH 6, and 60–70% at pH 7–12, indicating a dominance of charge repulsion while being ineffective in meeting the guideline of 1.5 mg/L. Increase in ionic strength led to a significant decline in retention of F (from 70 to 50%) and electrical conductivity (from 60 to 10%) by NF270, presumably due to charge screening. In contrast, BW30 retained about 50% of F at pH 3, >80% at pH 4, and about 99% at pH > 5, due to the smaller pore size and hence a more dominant size exclusion. In consequence, only little impact of ionic strength increase was observed for BW30. The concentration of NOM in permeates of both NF270 and BW30 were typically <2 mg/L. This was not affected by pH or ionic strength due to the fact that the bulk of NOM was rejected by both membranes through size exclusion.

The research is carried out in the context of providing safe drinking water for rural and remote communities where infrastructure is lacking, and water quality varies significantly. While other studies focus on energy

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[*] Corresponding author at: Membrane Technology Department, Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.
E-mail address: Andrea.Iris.Schaefer@kit.edu (A.I. Schäfer).

[1] Current address: Centre for Advanced Separations Engineering, University of Bath, Bath BA2 7AY, United Kingdom.

https://doi.org/10.1016/j.scitotenv.2017.11.111

fluctuations, this research emphasises on feed water quality that affects system performance and may alter due to a number of environmental factors.

1. Introduction

Fluoride (F) and natural organic matter (NOM) are two major contaminants in natural waters (both surface- and ground waters) in many developing countries such as Tanzania (Aschermann et al., 2016; Bretzler and Johnson, 2015; Fawell et al., 2013; Nanyaro et al., 1984). Although, a moderate concentration of F in drinking water (≈1 mg/L) is beneficial to human dental health (Fawell et al., 2006), concentrations above the World Health Organization (WHO) guideline value of 1.5 mg/L in drinking water can lead to serious health problems like dental and skeletal fluorosis (Fewtrell et al., 2006). The tolerable intake of F is lower in children as the tooth enamel is less developed than adults and therefore removing F below the guideline value is critical for children's healthy development (Eawag, 2015). NOM affects the aesthetic quality of the water; is a precursor for carcinogenic disinfection byproducts such as trihalomethane (THM); and may contribute to microbial (re)growth (Environmental Protection Agency Ireland, 2012; Meylan et al., 2007).

However, developing countries face particular infrastructure challenges relating to the provision of clean drinking water and electricity (The World Bank Group, 2017; World Health Organization, 2012). While clearly being 'advanced' technologies, membrane processes like nanofiltration (NF) and reverse osmosis (RO) are established water treatment options where dissolved contaminants need removal. Effective removal of inorganic and organic contaminants (e.g. F and NOM) and simultaneous pathogen removal render this an ideal solution for developing countries (Ayoob et al., 2008; García-Vaquero et al., 2014; Meenakshi and Maheshwari, 2006), in particular when coupled with renewable energies (Thomson and Infield, 2003). The economic aspect of a technology is a crucial factor for its implementation. It has been shown that the costs of water produced by renewable energy powered membrane technology are comparable to the prices of improved but untreated water in developing countries. In Tanzania, for example, people can pay as much as \$12 per m^3 for water from a kiosk, whereas the price of water produced by a membrane system (brackish water NF/RO with ultrafiltration (UF) as pre-treatment) powered by photovoltaics is estimated around \$6 per m^3 (Schäfer et al., 2014). This makes renewable energy powered membrane technology a viable treatment option for providing safe drinking water in developing countries where dissolved contaminants are to be removed, while physical disinfection can be easily achieved with much less energy-intensive processes such as UF.

F and NOM removal by NF/RO involve different mechanisms and therefore may be influenced by a number of water quality parameters, such as feed concentration, pH, ionic strength of the water as well as inorganic contaminant speciation and organic matter characteristics (Braghetta et al., 1997; Hu and Dickson, 2006; Meylan et al., 2007; Shen and Schäfer, 2015). Fluoride retention by NF/RO is generally controlled by steric (size exclusion) and electrical (charge repulsion, Donnan exclusion and dielectric exclusion) effects, while NOM is retained predominately due to size exclusion (Shen and Schäfer, 2015; Winter et al., 2017). To ascertain the robustness of NF/RO within the scope of varying water quality and environmental conditions such variants require investigation.

The pH and ionic strength of natural waters can vary significantly. Waters in one of the regions with the world's highest fluoride concentrations, the East African Rift Valley, are characterized by neutral and alkaline pH (Gizaw, 1996), while acid deposition from both natural and anthropogenic sources may lead to acidification (Gorham et al., 1986). High acidity in natural waters may stem from geochemical and biological causes including volcanic activity, hydrolysis of salts of heavy metal, excretion of acids by plants, organic acids from peat and bacterial activities (Baas Becking, 1938; Gorham et al., 1986). A natural water pH variation between 4 and 10 was observed in Ghana (Rossiter et al., 2010). Equally, natural waters occur with varying ionic strength with the main reasons for variation due to rising sea-levels, seawater intrusion and climate change (Vineis et al., 2011). In Tanzania for instance, natural waters with elevated F and NOM concentrations have variable ionic strength (tests were performed with waters of electrical conductivity (EC) between 314 and 16,150 μS/cm), while in soda lakes and some groundwater ionic strength was beyond seawater concentrations (Shen and Schäfer, 2015).

Water pH influences membrane properties, in particular surface charge, which is positive below the isoelectric point (IEP) and negative above, as well as F speciation (Childress and Elimelech, 1996; Dalwani et al., 2011; Deng et al., 2011; Mänttäri et al., 2006). Some authors reported that the pore size of membranes such as the NF270 increased at higher pH, which was explained by the greater intramembrane electrostatic repulsion (Teixeira et al., 2005), while another study did not confirm this with a number of NF/RO membranes including BW30 and NF90 (Richards et al., 2010). Ionic strength also affects the membrane surface properties. It is well understood that an increase in the solution ionic strength will compress the double layer of the charged solute or the charged membrane surface, which reduces the electrostatic interactions between these two entities (Childress and Elimelech, 1996; Tu et al., 2011).

At low pH, F exists as uncharged HF which dissociates to F^- above the pKa of 3.2 (Lide, 2008), and this speciation affects F charge and hydrated radius (Owusu-Agyeman et al., 2017). Naturally, this significantly affects F retention mechanisms. At high pH, however, the effect of pH on the retention of the charged F^- was reported to be low (Hoinkis et al., 2011). Ionic strength will affect F retention of charged species due to charge screening and Donnan effect (Luo and Wan, 2013; Tanninen et al., 2006; Zaidi et al., 2015). It has been reported that F retention by the NF270 membrane reduced from 70 to 20% with an increase in ionic strength from 0 to 850 mM as NaCl (Tanninen et al., 2006).

The structure of NOM is pH and ionic strength dependent. At low pH or high salt concentration, NOM is curled due to intra-molecular bonding while at low salt concentration and high pH is linear due to charge repulsion (Ghosh and Schnitzer, 1980). High ionic strength and low pH lead to a decrease in retention of NOM due to a combination of changes in charge repulsion and size exclusion (Braghetta et al., 1997; Kilduff et al., 2004; Luo and Wan, 2011). An increase in pH yielded higher NOM rejections due to pore narrowing, larger NOM hydrodynamic radius and stronger repulsions between the negatively charged membrane and NOM functional groups (Teixeira and Rosa, 2006). On the contrary, a decrease in pH from 10 to 4 led to an increase in permeate NOM concentration (as TOC) from 0.06 to 1.9 mg/L, whereas an increase in ionic strength from 1.6 to 61 mM resulted in an increase in permeate NOM from 0.5 to 1.4 mg/L (Braghetta et al., 1997). The result was explained with charge repulsion. In a study using natural water, an increase in ionic strength from 4 to 100 mM resulted in a 20% flux decline, the fouling being explained by the cake filtration model in which an increase in ionic strength led to a reduction of charge repulsion and increased accumulation of NOM molecules on the membrane surface (Jarusutthirak et al., 2007). Flux decline being more pronounced