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Change in performances and structure of RO membrane after chloramination in pure water, synthetic and natural seawater

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Reverse Osmosis (RO) filtration is a leading technology for desalination of seawater and brackish water. To avoid biofouling, continuous disinfection would be the most appropriate option, however it is known that polymeric membrane can suffer from the presence of remaining oxidant. The formation of disinfection by-products during the process may also damage the membrane. Accordingly, the physical chemical properties of the membrane and consequently its efficiency are altered.

The active layers of most commercial RO membranes are made of fully aromatic polyamide (PA), structure highly reactive with strong oxidant, e.g chlorine. Monochloramine that exerts significant lower oxidizing power may have potential to effectively control biofouling without damaging the membrane active layer. However, integrity loss of RO membrane can take place in the presence of combined chlorine, possibly as a result of catalytic reaction involving metal. High iodide and bromide concentrations are known to favor the production of more active haloamine species e.g. secondary oxidizing agents. The formation of these agents and of disinfection by-products (DBP) during the chloramination of seawater and brackish water can also contribute to the degradation of the membrane active layer.

The objective of this work is to explore the impact of chloramine exposure on the performances and structure of a polyamide membrane. Experiments were performed in pure, synthetic or natural seawater. The impact of the oxidant is studied by measuring the specific salt rejection and by monitoring the permeate flow under controlled operating conditions. The modification of the membrane structure (i.e. halogen substitution, oxidation) is examined using sophisticated characterization tools (RBS, ATR-FTIR).

Experiments are performed with a thin film composite (TFC) RO membrane with polyamide active layer (SW30HR, Dow FilmTec Co., USA). Preformed monochloramine is made by the slow addition at pH 8 of a solution of hypochlorous acid into a solution of ammonium chloride at high stirring rate. Nitrogen to chlorine (N/Cl) molar ratio is fixed at 1.2 in order to convert practically all the free chlorine to monochloramine. Solutions are prepared by dilution and dissolution of analytical grade reagent (NaOCl, NH₄Cl ACS reagent sigma Aldrich) with purified water produced by a Millipore system. The resistivity of t

he water is 18.2 MΩcm.

Two sets of experiment were conducted. The first one was performed in buffered MQ water (pH 8, 25°C, Phosphate buffer: 10 mM) by soaking membrane coupons in batch reactor at medium (20 ppm as Cl₂) and high initial chloramine concentration (500 ppm as Cl₂).

Change in the membrane performances and structure are evaluated based on CT exposure going up to 90 000 ppm.h as Cl₂. The second one was operated under semi-continuous mode (i.e. recirculation of the chloraminated solution using unpressurized cell without permeation) with buffered MQ water, synthetic and natural seawater (Red Sea water).

As to compare with the previous static mode, only the surface in direct contact with the solution is subjected (expected) to the oxidant. With the objective to remain as close as possible to the normal treatment conditions, a concentration of 20 ppm as Cl₂ of monochloramine is used. Because monochloramine is not stable in the presence of high concentration of bromide, a fresh solution of monochloramine at pH8 is prepared every 48 hours. Target CT for recirculation mode experiment are 2500, 6000 and 10 000 ppm.h as Cl₂, the longest CT representing 60 days of operation.

During all experiments the decay of chloramines content is followed to determine true applied CT.

Rejection efficiency and permeability of the treated membrane are determined under similar conditions (25°C, TDS=35 g/L prepared with pure analytical reagent salts, TMP=55 bars) after loading the treated coupons in a high pressure RO unit (SIMATec RO unit) equipped with conductivity cells to determine the total salt rejection. Samples are also analyzed by ion chromatography for the determination of specific rejections for Cl⁻, SO₄²⁻ and Br⁻. The monitoring of specific rejection will allow us to better follow the change in transport mechanism (advection or diffusion) and the solute permeability coefficient B used to characterize membrane.

The modification of polymer composition was studied on the chloraminated coupons using FTIR and RBS analyses.

The NH₂Cl exposure in buffered MQ (pH8) water at initial concentration of 500 ppm leads to an increase of the membrane permeability with increasing CT. The normalized permeability reaches a plateau at 1.7 for a CT of 20 000 ppm.h. A linear decrease of total rejection is also noticed at a rate of -8×10^{-8} ppm⁻¹.h⁻¹ (Normalized rejection versus CT). FTIR and RBS spectra of exposed membrane coupons were compared to virgin and chlorinated membrane coupons and showed qualitatively different evolution, observation that seems to indicate that the reaction mechanisms involved in the degradation process are different for HOCl and NH₂Cl.

The impact of the mode of chloramine exposure (batch vs recirculation) was investigated using chloraminated MilliQ water at pH8. For a CT of 2500 ppm.h (initial concentration at 20 ppm during 180 hours), the final normalized permeability for batch, recirculation on polyamide (PA) surface and polysulfone (PSf) surface are 1.40, 1.54 and 1.13, respectively. These results show that the chloramination of the PSf layer does not have major impact on the permeability of the membrane. On the contrary monochloramine alter the membrane properties; a stronger impact being observed with the recirculation mode. The difference may be due to a more targeted reactivity of monochloramine with the PA surface in the recirculation mode as compared to the batch mode (higher "true" CT).

Long-term experiments are performed with 4 recirculation cells operated in parallel. The cells loaded with SW30HR membrane coupons are operated with chloraminated MilliQ water (duplicate), synthetic seawater and Red Sea water. Experiments are still in progress; a CT exposure of 6000 ppm.h was obtained few days ago. Several more weeks are required to reach the goal of 10,000 ppm.h. It is expected that the results will provide information on the impact of NOM during the chloramination of membrane fed by seawater.

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