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Characterization and removal of disinfection by-product precursors by resins – Literature review and pilot tests

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Summary:

This work provides the key results of a literature review assessing the resin fractionation processes to study the disinfection by-products precursors. A practical case is also presented. Fluidized bed column experiments have been performed to assess the efficiency of 4 ion exchange resins in terms of DBP precursor removal. DOC removal, including the different fractions determined by size exclusion chromatography-carbon detector, 10 THMs and 7 HAAs have been measured and compared. IEX resins lowering iodide and specific precursors showed a high capacity in lowering the formation of I-THMs. However, additional experiments with increasing halide concentrations showed the limitations of IEX process to limit the DBP formation.

Keywords: IEX, natural organic matter, disinfection by-product formation potential

INTRODUCTION

Ion exchange processes (IEX) are used in drinking water treatment to remove dissolved organic matter with industrial application starting from the 2000s (Levchuk et al., 2018). Ion exchange is of particular interest as a pre-treatment before coagulation as it has been shown to significantly reduce the coagulant dose required (by 50 to more than 80 %) (Grefte et al., 2013). Using IEX in combination with coagulation, can thus remove both a higher amount of dissolved organic carbon (DOC), and a broader spectrum of DOC as hydrophilic and low molecular weight fractions (LMW) fractions are more difficult to remove using conventional coagulation treatment. IEX can then be an interesting process helping to control the formation of disinfection by-product (Watson et al., 2015). Furthermore, anionic resins can also remove bromide from certain water sources with low alkalinity (Watson et al., 2015), thereby potentially reducing the formation of brominated DBPs during disinfection (MacKeown et al., 2021).

From an analytical point of view, numerous researches have been conducted on NOM separation and extraction with resins based on ion exchange and hydrophobic interactions. We performed a work of review to assess the use of these techniques for obtaining specific fractions and to characterize their reactivity as DBP precursors during chlorination. We completed our study by assessing the removal of DBP precursors from raw surface water used for drinking water production on four different ion exchange resins in a fluidized bed column test. The interest of the IEX process in different scenarios of increasing halide concentrations has been studied in

order to evaluate such processes on raw water impacted by high levels of halides and to gain more knowledge on DBP precursors.

MATERIALS AND METHODS

Pilot tests have been conducted on a raw surface water used as a drinking water resource ($40\,000\text{ m}^3\text{ day}^{-1}$). The water is characterized by a high NOM content, with an average DOC content of 12 mgC L^{-1} , combined with a high alkalinity and hardness. Due to the combination of high DOC concentration and relatively high alkalinity, the water requires large amounts of coagulant and sulfuric acid during coagulation. The four resins tested were Purolite PPA860S, Dowex TAN-1, Amberlite IRA-958 and Amberlite IRA-410. The three first mentioned resins are strong base anion type I resins with a quaternary ammonium group, and the last one is a strong base type II resin where a methyl group is replaced with an alcohol group. The pilot test experiments are presented in details in MacKeown et al. (2021).

10 THMs and 7 HAAs have been analysed by the high sensitivity headspace-trap methods GC-MS developed in our laboratory (MacKeown et al., 2020).

RESULTS AND DISCUSSION

I. Evaluation of resin NOM fractionation in the assesment of DBP precursors

From our work of literature review dealing with the DBP formation potential (DBP FP) of NOM fractions obtained by resin treatment, we were able to draw some trends despite the broad and sometimes contradictory results. An example is given in Figure 1.

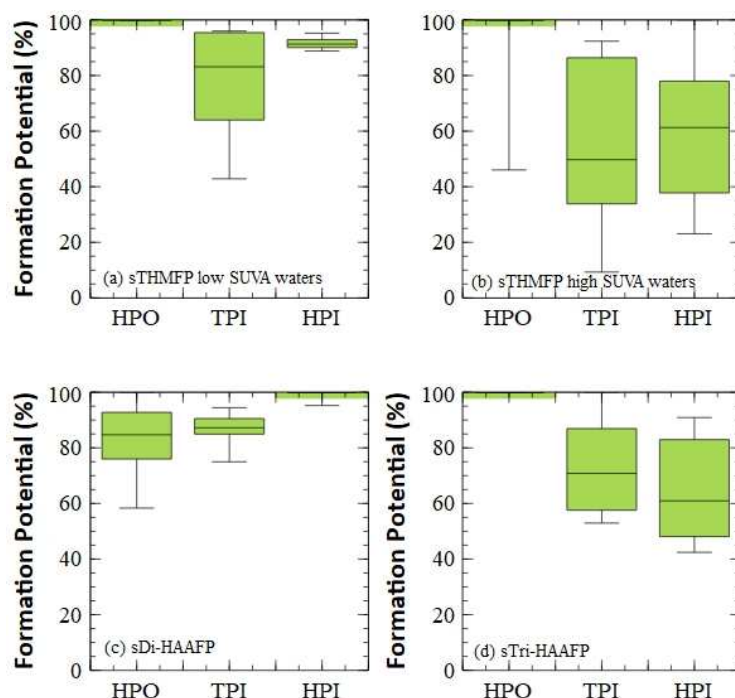


Figure 1: Disinfection by-product formation potential in hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions. For each water sample, the highest formation potential has been defined as 100% and the other formation potentials have been recalculated based on the highest formation potential; (a) THMFP for low SUVA_{254} waters, (b) THMFP for high SUVA_{254} water, (c) Di-HAAFP, (d) Tri-HAAFP (total of 26 datapoints). The whiskers represent the minimum and maximum of all datapoints. The boxplot itself is ranged within the 1st and 3rd quartile (25th and 75th percentile) with a horizontal line for the 2nd quartile (median).

Whatever the distinction between 2 (hydrophobic/hydrophilic) or 3 fractions (additional transphilic fraction), the hydrophobic fraction (HPO) is always the highest THM4 precursors. However, a distinction could be made for the high and low SUVA waters. In fact, the contribution of HPI (hydrophilic) and TPI (transphilic) fractions in low SUVA ($< 2.0 \text{ L mg}^{-1}\text{m}^{-1}$) water are not far below the one of HPO (the median values show a reduction of maximum 20% in the formation potential from HPI and TPI compared to HPO, the highest contributor). The difference is much higher in high SUVA waters ($> 2.8 \text{ L mg}^{-1}\text{m}^{-1}$) from the different studies reviewed. A different trend could be seen for the HAA FP, with small differences between fractions, HPI tending to be the highest precursors of di-HAAs while HPO is the highest contributor of tri-HAA formation.

II. Ion exchange pilot treatment

The treatment of raw water by ion exchange removed from 23 up to 41 % of the dissolved organic carbon content based on DOC measurement depending on the type of resins (Figure 2). A poorer result of DOC removal compared to the manufacturer information is obtained, which could be due to the high concentration of sulfate ion (104 mgL^{-1}) which compete with the exchange sites. In addition, the low SUVA NOM could also be a poor target of exchange sites.

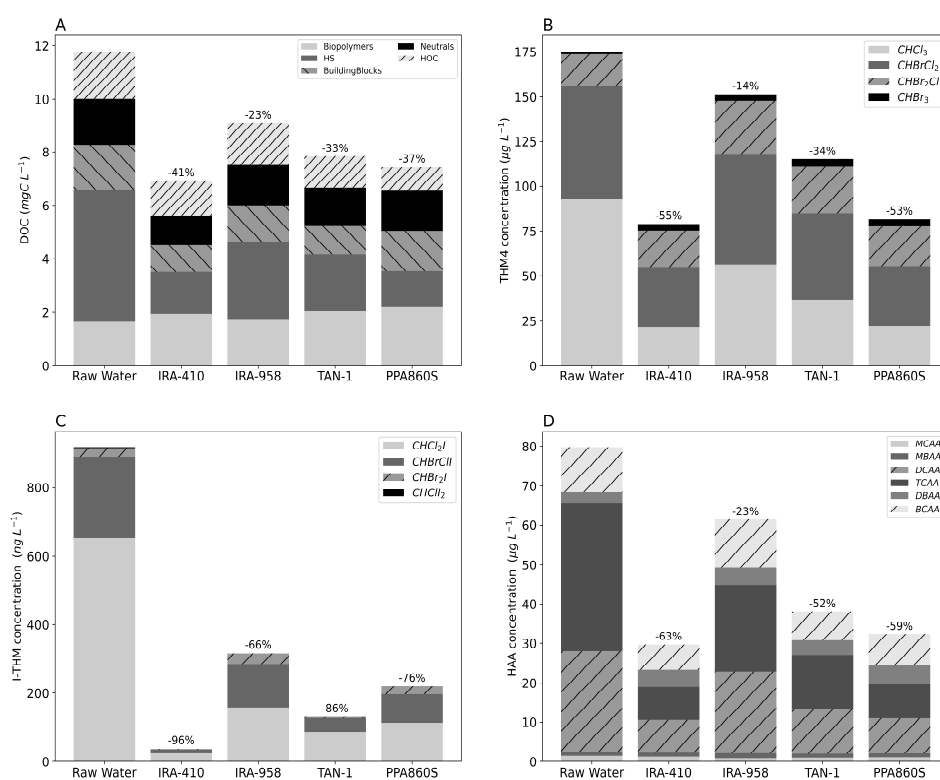


Figure 1: Assessment of IEX process efficiency for the 4 different resins compared to raw water for dissolved organic carbon removal and disinfection by-product formation potential (24 h – low chlorine residual). A) NOM fraction removal assessed by LC-OCD B) THM4, C) I-THMs and D) HAAs. Numbers above bars correspond to the reduction percentage compared to the concentration of each parameter in raw water (MacKeown et al., 2021).

In terms of disinfection by-product formation potential, 7-days and 24-hours tests show different results allowing to make a distinction in terms of fast and slow reacting precursors. Additional experiments have been performed with increasing

concentration of bromide and iodide. IEX resins exhibit a preferential removal of DBP precursors which have a slow reactivity towards chlorination and THM formation. In comparison with THM₄, the reduction in I-THMFP compared to raw water is 2 to 10 times higher, in the range 76–96 % and much higher than the DOC removal. This behaviour is only partially explained by the removal of iodide, then, the removal of specific reactive precursors has to be supposed.

All resins showed a beneficial effect in lowering the concentration of I-DBPs by lowering iodide and/or by the removing of specific precursors. Finally, the advantage of DBP reduction by the IEX treatment is however reduced in presence of an increasing concentration of halides. The reduction of efficiency is highly dependent on the resin type. Results are discussed for the different resins and is also compared with the performance of a full-scale classical treatment plant.

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