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Insights into biopolymer and humics natural organic matter removal mechanisms by anion exchange resins

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ABSTRACT

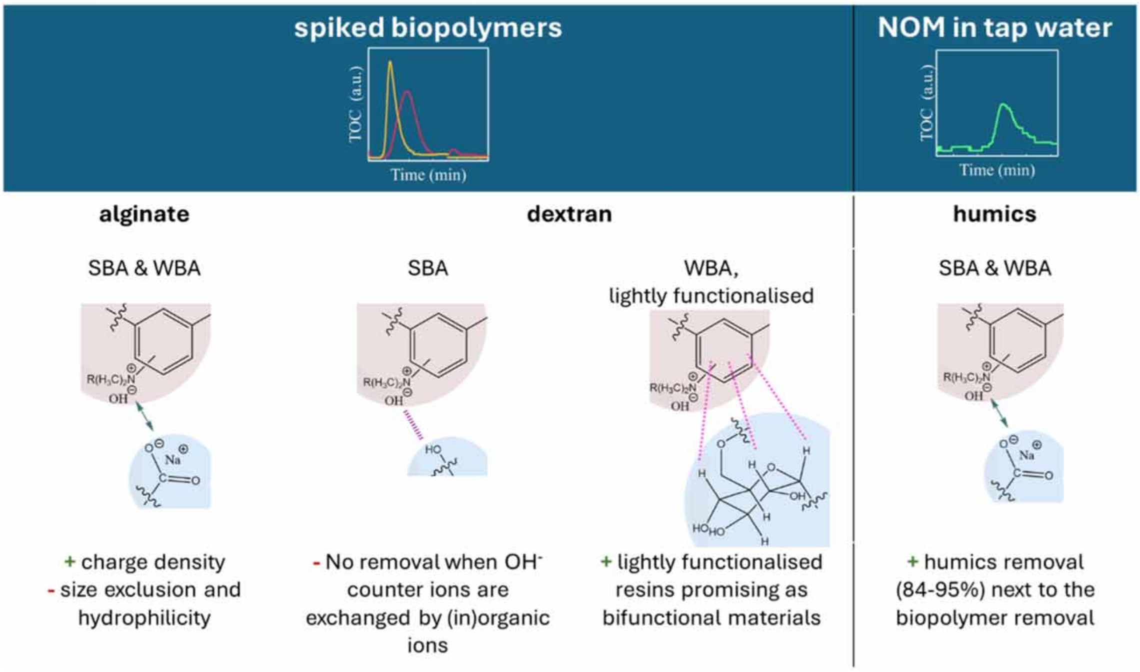
Biopolymer natural organic matter is linked to different issues during water treatment, such as membrane fouling, and their complete removal, is still challenging. In this work, the removal of biopolymer surrogates (uncharged dextran and anionic alginate) was investigated with weak (WBA) and strong (SBA) basic anion exchange resins. These surrogates were introduced into ultra-pure (UP) and tap water to assess the impact of a complex water matrix on their removal. Additionally, the study explored the removal of naturally occurring humic substances present in tap water. Alginate exhibited moderate removal through ion exchange with WBA and SBA resins in both water matrices. A significantly higher removal efficiency for humics was obtained through the same removal mechanism, linked to the smaller size and higher hydrophobicity of humics. SBA resins with OH– counter ions removed up to 95% of dextran from UP water by H-bonding, while ions present in tap water excluded this interaction. The lightly functionalised WBA resin SD-2 achieved a dextran removal of 50 and 60% from tap and UP water, respectively, via CH–π interactions with the resin matrix. The latter results demonstrate that resins with lower capacities are promising to optimise interactions with both the matrix and functionalities.

Key words: adsorption, alginate, dextran, HPSEC-UV-TOC, ion exchange, water treatment

HIGHLIGHTS

- Efficient removal of uncharged biopolymer from ultra-pure water by strongly basic anion exchange resin in OH^- form
- Water matrix influences removal mechanism and efficiency, especially for uncharged natural organic matter (NOM).
- NOM characteristics strongly affect its removal by ion exchange.
- Lightly functionalized anion exchange resins promising for simultaneous removal of uncharged biopolymers and anionic humics.

GRAPHICAL ABSTRACT



INTRODUCTION

The depletion of groundwater results in a shift from the use of ground to surface water as a resource for industrial or drinking water production processes. However, the composition and characteristics of the latter are more challenging due to, e.g. its elevated concentration and variation of natural organic matter (NOM) and the presence of a biopolymer (BP) NOM fraction in surface water. This affects both quality and, consequently, the water treatment processes used in this context (Brezinski & Gorczyca 2019).

Conventional water treatment processes are commonly based on coagulation/flocculation, rapid or slow sand filtration, and adsorption on activated carbon, and have proven their effectiveness in removing a substantial amount of NOM from water (Matilainen *et al.* 2010; Levchuk *et al.* 2018). Several recent studies have highlighted the high effectiveness of ion exchange (IEX), particularly utilizing anion exchange resins (AER) for an improved removal of NOM from water. Additionally, it was shown that when AER is applied as a pretreatment method before coagulation, a reduction of the amount of coagulant needed and an improved overall NOM removal is obtained (Finkbeiner *et al.* 2018; Caltran *et al.* 2020; MacKeown *et al.* 2021). When AER are applied in a demineralisation unit combined with cation exchange resins, the AER not only removes inorganic anions from surface water but it was shown that a NOM removal exceeding 90% was accomplished as well (De Meyer *et al.* 2019).

The good overall NOM removal with AER resins can be explained by the NOM composition and characteristics. NOM is a complex mixture of molecules with different functionalities and covering wide ranges of hydrophobicity and molecular weights (Bhatnagar & Sillanpaa 2017). Different NOM classification systems have been developed to define NOM fractions based on a selection of chosen properties, of which the most commonly used ones are resin fractionation (based on hydrophobicity and acidity (Leenheer 1981)) and liquid chromatography coupled with organic carbon detection (LC-OCD, based on molecular weight (MW) combined with acidity (Huber *et al.* 2011)). LC-OCD classifies NOM in five fractions: the high MW biopolymers (BP; $MW > 10$ kDa), medium MW humic substances (HS), and building blocks (BB) of these HS ($10\text{ kDa} > MW > 0.4\text{ kDa}$), low MW acids and neutrals (LMWA and LMWN, respectively, $MW < 0.4$ kDa). Of these fractions, the HS are the most abundant, accounting for 50–90% of the NOM, depending on the water source (Thurman 1985; Ding *et al.* 2022). These HS are anionic at neutral pH, which explains their good removal by AER.

Complete removal of all NOM fractions from water is, however, still not achieved by any of the conventional treatment processes or by commonly used IEX processes. Especially the fractions having a relatively low charge density, such as the BP, which primarily comprises polysaccharides and proteins, are challenging (Bazri *et al.* 2016; Finkbeiner *et al.* 2018; Galjaard *et al.* 2018; De Meyer *et al.* 2019; Caltran *et al.* 2020; Fernandez *et al.*

2021). Remaining BP causes issues in downstream processes such as steam circuit corrosion (De Meyer *et al.* 2019) or fouling of membranes (Yamamura *et al.* 2014), illustrating the value of a targeted removal approach for this specific fraction, in addition to a good overall NOM removal by AER.

Moreover, there is a notable gap in the existing literature when it comes to thoroughly studying how hydrophilic, high MW anionic molecules interact with AER. The emphasis in current literature primarily revolves around (surrogates for) the relatively hydrophobic anionic HS. However, when comparing SUVA values (specific UV absorbance at 254 nm divided by the dissolved organic carbon (DOC) concentration) in various surface waters with commonly used surrogates for HS like humic acid, it can be noticed that NOM or HS in surface water possesses less aromaticity and is consequently less hydrophobic compared to the used surrogate (see Supplementary Information, Table S1). This distinction could introduce bias into conclusions drawn regarding aspects such as the removal efficacy or the interactions between these surrogates and the real HS NOM fraction with AER or other water treatment techniques. This underscores the significance of conducting experiments with model compounds encompassing a broad spectrum of characteristics, or when possible, real NOM fractions.

In our previous work, five different NOM surrogates were spiked in ultra-pure (UP) water to gain fundamental insights into the removal mechanisms and efficiency of these surrogates with AER (Laforce *et al.* 2022). Additionally, the effect of the resin conditioning to a specific counter ion (OH^- (or free base (FB) in the case of weak basic AER) and Cl^-) on the equilibrium pH and subsequent NOM surrogate removal in batch experiments was investigated. It was found that both the type of AER (strong (SBA), weak (WBA), or mixed (W/SBA) basic functionality) and the resin conditioning affect its effectiveness in removing a specific NOM surrogate from UP water. For anionic surrogate molecules, ion exchange was the main contributing removal mechanism. Uncharged NOM having hydroxyl groups, such as (poly)saccharides, were efficiently removed by SBA resins in the OH^- counterions form but poorly in the Cl^- form, which was explained by H-bonding between the hydroxyl groups and the OH^- counter ions as dominant removal mechanisms.

However, the use of UP water spiked with NOM surrogates is a simplified representation of the actual composition of a water sample. In real water samples, NOM is usually present in relatively low concentrations and the water matrix contains both organic and inorganic contaminants. In this study, polysaccharide BP surrogates (dextran and alginate) were spiked in tap water to study the effect of the water matrix (UP vs. tap water) on the removal of NOM by AER. Moreover, the removal of humics from tap water, next to the surrogate removal, was studied in the spiking experiments with tap water. An SBA resin in both OH^- and Cl^- form and a WBA resin in Cl^- form were used to study the removal of the high MW, hydrophilic, and anionic NOM surrogate alginate. For the uncharged polysaccharide dextran, an SBA (OH^-) resin and a lightly functionalised WBA (FB) resin, having a high porosity and thus a more open structure, were selected. Especially for larger molecules, which are hindered in migrating to the resin matrix, a lower ion exchange capacity and more open structure could be beneficial. Our previous research demonstrated the effective removal of dextran by styrene adsorber resins through CH–π interactions between the axial positioned H-atoms of dextran and the π-electron system of the aromatic resin matrix (Laforce *et al.* 2022). These interactions were, however, impeded by steric hindrance in the case of AER with a styrene matrix. Here, it was tested if dextran can be removed by interactions with the matrix of a lightly functionalised AER, where steric hindrance is limited.

The aim of the experiments conducted in this work was to gain (1) a better understanding of the removal efficiency and mechanisms of BP NOM by AER from real water samples with a complex water matrix and (2) an improved insight into the overall NOM removal potential, which is related to the humics removal, of the used AER.

METHODS

NOM surrogates and water sources

The relatively low concentration of BP NOM in many surface waters challenges an accurate concentration measure of raw and treated water. For this reason, two surrogates for the BP NOM fraction were selected. Since polysaccharides are the major constituents of BP in surface water, the chosen surrogates in this work both belong to this class of BP. Dextran (from *Leuconostoc* spp., Sigma Aldrich), having a $pK_{a,1}$ of 12.3, was used as a surrogate for the uncharged polysaccharide BP fraction. Dextran is a homopolysaccharide of glucose, consisting of mainly linear α $(1 \rightarrow 6)$ and about 5% branched α $(1 \rightarrow 3)$ links. Sodium alginate (Sigma Aldrich) is an anionic polysaccharide, containing α-L-guluronic acids (GulA) and β-D-mannuronic acids (ManA) building blocks and has a $pK_{a,1}$ of 3.2 (Draget *et al.* 1994). Alginate was selected as a surrogate for hydrophilic high MW anionic compounds. This BP NOM surrogate is frequently used in studies on the fouling mechanisms of BP in membrane filtration (Guo *et al.* 2009; Hashino *et al.* 2011; Cheng *et al.* 2016; Motsa *et al.* 2018). These studies typically spike the surrogate molecules into UP water. Few researchers have adapted the water matrix to better mimic the water matrix of real water sources, or to study the influence of the water matrix on alginate. For example, Hashino *et al.* (2011) used a bicarbonate buffer to maintain a controlled pH of 8 during membrane fouling experiments. Motsa *et al.* (2018) examined the effect of different parameters, such as the ionic strength of the solution, on alginate characteristics like hydrodynamic volume and its related influence on fouling behaviour. The removal of alginate by AER has been studied only to a limited extent, using UP water (Laforce *et al.* 2022).

The chemical structures of the building blocks of dextran and alginate are shown in Figure 1. The addition of dextran or alginate to the tap water is not anticipated to significantly impact its bacterial community (BC), since the growth rate of the BC in tap water is usually constant and carbon-limited. The assimilable organic carbon fraction of the organic carbon pool does typically not comprise polymers. Hence, the spiked biopolymers are not expected to significantly influence the BC or its growth rate in tap water (Vital *et al.* 2012).

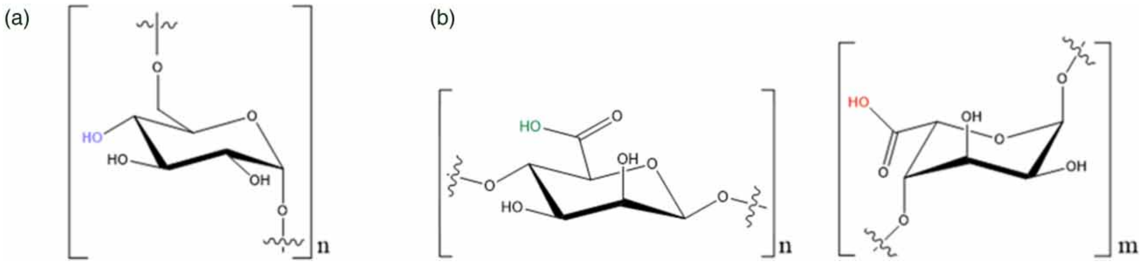


Figure 1 | Chemical structure of the building blocks of dextran (a) and protonated alginate (b).

Synthetic water solutions were prepared by spiking 8 mg L^{-1} dextran or sodium alginate into UP or tap water. The UP water was produced from demineralized water using a Milli-Q water purification system from Merck and had a pH of about 6.5 and a total organic carbon (TOC) content below 50 μgC L^{-1}. The tap water (potable water produced by Farys Belgium, delivery area 2) contained about 1.50 mg C L^{-1} NOM (measured via HPSEC-TOC analyses, see Section 2.3), which mainly consisted of humics (1.30 mgC L^{-1}). These humics consist of a mixture of molecules having aromatic and aliphatic structures, containing different functional groups. Carboxylic (pK_a of about 4.7) and phenolic (pK_a of about 10.0) functionalities are the most abundant. Figure 2 shows possible humics constituents (humic and fulvic acid and carboxyl-rich alicyclic molecules). General tap water characteristics can be found in Table 1.

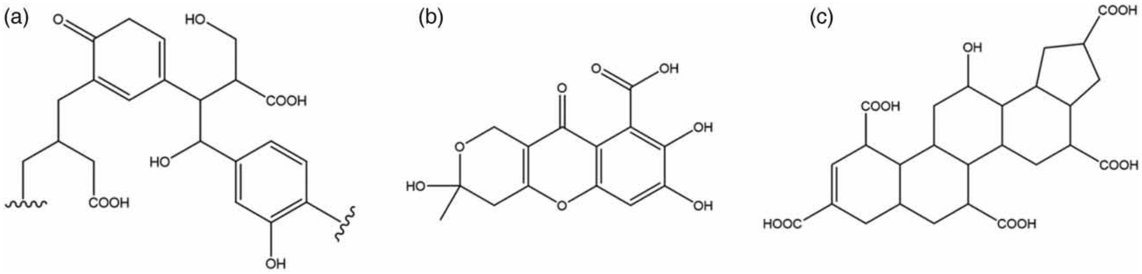


Figure 2 | Representation of HS NOM building blocks or constituents with (a) a humic acid structure based on (Al-Faiyz 2017), (b) fulvic acid ('PubChem Compound Summary for CID 5359407, Fulvic acid' 2023), and (c) a carboxyl-rich alicyclic molecules structure based on Sleighter & Hatcher (2008).

Resins and pretreatment

An SBA resin (MP500) conditioned to its OH^- counterion form was selected for the dextran removal experiments. Experiments with the Cl^- counterion form of this resin were not conducted, since previous work

Table 1 | General tap water characteristics from Farys Belgium (delivery area 2) (Farys 2023)

Parameter (unit)	Average value	Parameter (unit)	Average value
pH (–)	7.8 ± 0.2	Sodium (mg L^{-1})	37 ± 12
Conductivity (μS cm^{-1})	552 ± 117	Potassium (mg L^{-1})	6 ± 3
Inorganic carbon (mg HCO_3^- L^{-1})	200 ± 52	Calcium (mg L^{-1})	79 ± 28
Sulphate (mg L^{-1})	73 ± 17	Magnesium (mg L^{-1})	10 ± 4
Chloride (mg L^{-1})	61 ± 31		

showed that dextran was only successfully removed by IEX resins by H-bonding with the OH^- counterions of SBA resins (Laforce *et al.* 2022). Additionally, SD-2, a lightly functionalised WBA polystyrene (PS) adsorber resin in its FB form, was chosen for the dextran experiments.

SBA MP500 (OH^- and Cl^-) and WBA MP62 (Cl^-) were selected to study both the effect of functionality and counter ion on the alginate removal. The washing and conditioning procedures for all resins and counterion forms are described in Laforce *et al.* (2022). The main properties of the selected resins and the conditioning solution used to obtain the desired counter ion form are given in Table 2. The difference in capacity between the OH^- and Cl^- forms of the MP500 resin is explained by the distinct water content of both forms.

Table 2 | Main properties, conditioning solution, and respective counter ion form and capacity of the used AER

Resin	Matrix	Structure	Functionality	Form	Conditioning Solution (1 M)	Capacity[a]
SD-2[b]	PS-DVB[d]	MP	WBA	FB	NaOH	0.3
MP62[c]	PS-DVB	MP	WBA	Cl^-	HCl	1.6
MP500[c]	PS-DVB	MP	SBA (type I)	OH^-	NaOH	1.2
MP500[c]	PS-DVB	MP	SBA (type I)	Cl^-	HCl	1.3

[a] meq g^{-1} wet resin, determined via titrations according to the ASTM 2187-94 procedure.
[b] Amberlite, Dupont.
[c] Lewatit, Lanxess.
[d] Polystyrene crosslinked with divinylbenzene.

Batch ion exchange experiments and analysis

0.1 g of washed and conditioned wet resin in the FB or OH^- form, or a mass with equivalent capacity for the Cl^- form, was added to 50 mL spiked UP or tap water in a jar. The jars were shaken for 22 h at 200 rpm and 25 °C (infors HT Multitron Standard) until equilibrium was reached. The batch experiments were performed in duplicate, together with blanks (UP or tap water without spiked surrogate).

Initial and equilibrium pH was measured by an InoLab pH Level 1 m. The initial and equilibrium NOM fraction concentrations were determined with high-performance size exclusion chromatography (HPSEC-UV-TOC) analysis. The HPSEC-UV-TOC system consisted of an Agilent 1260 InfinityII HPLC equipped with a Toyopearl HW-50S SEC column, combined with a diode array detector (measuring the absorbance at 254 nm) and a Sievers M9 TOC detector. The used mobile phase (flow rate 1 mL min^{-1}) was a 4 mM phosphate buffer of pH 6.8 (2.4 mM NaH_2PO_4; VWR chemicals, p.a. and 1.6 mM Na_2HPO_4; Supelco, p.a.) with adapted ionic strength (25 mM Na_2SO_4; Supelco, p.a.). Before injecting the sample for analysis with the HPSEC system, the inorganic carbon was removed by adjusting the pH to 6 by use of a 1 M H_3PO_4 solution and degassing the sample with N_2-gas (Air Liquide) at 70 mL min^{-1} for at least 30 min (Laforce *et al.* 2024). Next, the sample is pre-treated with a 20-fold concentrated mobile phase solution to adjust the ionic strength of the samples with one of the mobile phases to suppress matrix effects. All samples were finally filtered with a 0.45 μm filter (Chromafil PET, Macherey-Nagel).

MW calibration of the HPSEC system was performed with pullulan standards (PSS, 180 Da–107 kDa), and calibration on organic carbon concentration was conducted using potassium hydrogen phthalate (Acros organics, p.a.) standard solutions with concentrations between 0.05 and 10.00 mgC L^{-1}. Detailed information on the principles and validation of the utilized HPSEC-TOC(-UV) method can be found elsewhere (Laforce *et al.* 2024). Three NOM fractions, defined as the high, medium, and low MW fractions, are distinguished in the HPSEC-UV-TOC chromatograms. The high MW fraction, also referred to as the BP fraction, consists of the spiked BP surrogate only in the case of the UP water experiments, and the surrogate combined with the BP present in the tap water for the tap water experiments. The latter are not considered in this work due to their low concentration (about 0.10 mgC L^{-1}) compared to the spiked surrogate concentration (8 mg L^{-1}). BP measurements and calculations are based on HPSEC-TOC data. The medium MW fraction, which is only discussed in the case of the tap water experiments, consists mainly of HS and their breakdown products (which have smaller molecular weights but similar chemical structures and functionalities) present in the tap water. LMWA also elutes in this range but have typically in very low concentrations (low ppb range). This fraction was measured via HPSEC-UV at 254 nm, and is referred to as the humics. The low MW fraction from the tap water was not considered in this work due to the low concentration (about 0.15 mgC L^{-1}) and the corresponding analytical challenges in accurately measuring the initial and equilibrium concentration of this fraction.

Removal efficiencies for the BP and humics were calculated with the following equation:

$$\text{Removal efficiency (\%)} = \frac{C_{\text{initial}} - C_{\text{equilibrium}}}{C_{\text{initial}}} * 100\ \% \tag{1}$$

with C_{initial} the initial concentration of BP (TOC) or humics (UV_{254}) and $C_{\text{equilibrium}}$ their concentration at equilibrium.

RESULTS AND DISCUSSION

Alginate spiking experiments

Figure 3 shows an overlay of the HPSEC-TOC chromatograms of tap water (black) and 8 mg L^{-1} alginate spiked in UP (yellow) and tap water (red) as well as the HPSEC-UV chromatogram of tap water (black, dashed line). Alginate elutes in the high MW BP integration range of the chromatogram (between about 25 and 40 min). No MW calculations for alginate could be made based on the HPSEC-TOC chromatogram since the elution time of the peak maximum of alginate corresponds to the size exclusion limit of the column, where all molecules with hydrodynamic volumes that are too big to enter the pores of the SEC resin elute. Moreover, the anionic character of alginate results in shorter elution times (Ruhl *et al.* 2012), which additionally complicates an accurate MW determination for this molecule. In the HPSEC-TOC chromatogram of the tap water, a very small peak can be noticed in the BP integration range, while no peak is observed in the HPSEC-UV (absorbance at

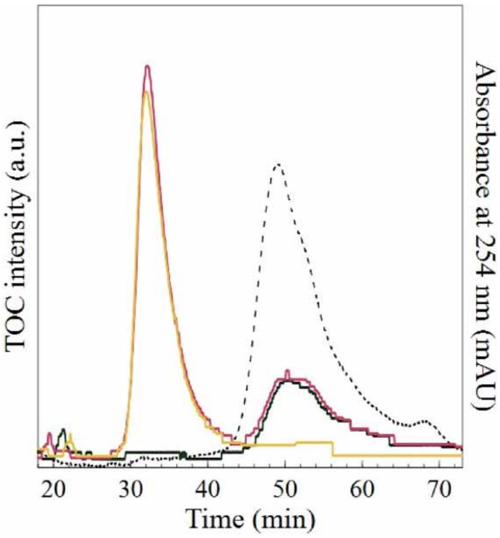


Figure 3 | Overlay of the HPSEC-TOC chromatograms of 8 mg L^{-1} alginate spiked in tap water (red) and UP water (yellow) and tap water as such (black), next to the HPSEC-UV chromatogram of tap water (dashed line).

254 nm) chromatogram in this range. This was explained by the aliphatic nature of the BP NOM fraction (Huber *et al.* 2011).

In the HPSEC-TOC chromatogram of alginate spiked in tap water, an additional peak can be noticed between about 40 and 65 min, which is not present in the chromatogram of alginate spiked in UP water. This additional peak comprises the humics, BB LMWA, and LMWN present in the tap water. In the discussion of this work, only the first part of this peak containing the humics, BB, and LMWA (from about 40–59.5 min, (Laforce *et al.* 2024)) was taken into account. The chromatogram illustrates that spiking alginate in tap water has no significant influence on the concentration or MW distribution of the humics.

The initial and equilibrium pH and the removal efficiency of AER MP500 (both OH^- and Cl^- form) and WBA MP62 (Cl^- form) for alginate from UP and tap water and humics from tap water are presented in Figure 4.

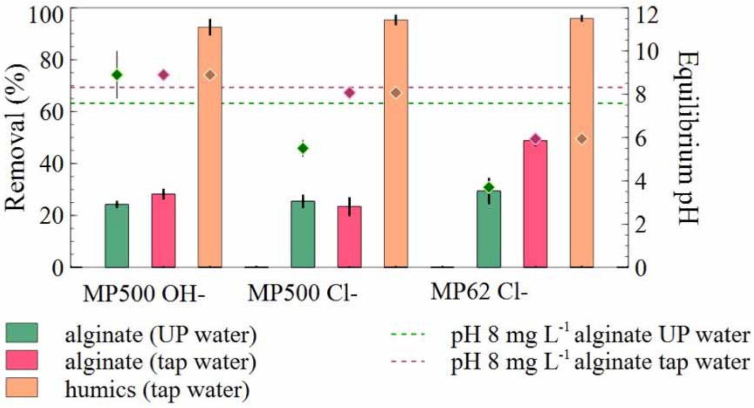


Figure 4 | Removal efficiency (bars) and equilibrium pH (dots) for alginate spiked in UP and tap water and humics from tap water (50 mL spiked water + 0.1 g NaOH conditioned resin (mass with equivalent capacity for HCl conditioned resin); 22 h, 200 rpm, 25 °C.

Alginate removal with SBA MP500 did not exceed 30% and showed no significant differences between the experiments with a different water matrix or counter ion. Ion exchange was proposed as the predominant removal mechanism for alginate by the SBA resin, as illustrated in Figure 5. Previous research indicated that charge density was the key factor in the removal of NOM surrogates via ion exchange from UP water by SBA resins (Finkbeiner *et al.* 2019). H-bonding between the hydroxyl groups on alginate and the OH^- counterion of the NaOH-conditioned resin can contribute to the alginate removal as well. However, the similar removal efficiency of both the OH^- and Cl^- counterion forms, confirmed the predominant removal mechanism was ion exchange. The presence of other (both inorganic and organic) anions in the tap water could affect the alginate removal, e.g. competition for available ion exchange sites (Liu *et al.* 2021). Moreover, Motsa *et al.* (2018) observed the complexation of alginate with calcium ions in a synthetic solution containing 80 mg L^{-1} alginate and 1 mM Ca^{2+}, which was illustrated by a fourfold increase of the hydrodynamic volume of alginate and approximately a fourfold decrease of the zeta potential compared to alginate spiked in UP without the addition of salts. Since the calculated charge density of alginate in our study is approximately 39 meq L^{-1}, while only

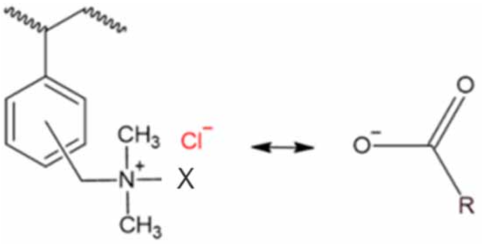


Figure 5 | Ion exchange (indicated by arrow) as a removal mechanism for molecules having a carboxyl functionality with an AER resin. For a WBA resin, X = H (at neutral to slightly acidic conditions), and for a SBA type I resin, X = CH_3 (at neutral to slightly acidic or basic conditions).

about 4 meq L^{-1} of calcium ions are present, a significant portion of the carboxyl functionalities of alginate remains available for ion exchange, which explains the removal by this mechanism. Changes in the hydrodynamic volume of alginate could not be deducted from the results of the HPSEC-TOC data in our study, since alginate elutes at the size exclusion limit of the column. However, the similar alginate removal in both UP and tap water, where the hydrodynamic volume is expected to be larger, indicates that alginate removal is limited to the outer surface of the resin in both cases.

The unaltered alginate removal in the presence of the naturally occurring humics in the tap water indicated a preferential removal of the alginate. This can be attributed to the high charge density of alginate, which contains one carboxyl group per monosaccharide unit ($C_6H_7O_7$), resulting in a calculated charge density of approximately 13.9 meq mgC^{-1}. In contrast, the proposed constituents of humics contain only one acid site per multiple aromatic or cycloaliphatic units, leading to much lower charge densities, such as 0.56 meq mgC^{-1} for tannic acid and 1.08 meq mgC^{-1} for pentagalloylglucose, which are both proposed humics constituents (Finkbeiner *et al.* 2019). Overall, it can be concluded that the alginate removal efficiency of MP500 (both OH^- and Cl^-) was not affected by the water matrix of the tap water at the used experimental conditions.

The equilibrium pH showed the same trend, caused by Donnan exclusion, as reported in our previous work (Laforce *et al.* 2022). The equilibrium pH of the MP500 (OH^-) experiment was higher than the initial pH while the equilibrium pH of the HCl-conditioned resins (MP500 (Cl^-) and MP62 (Cl^-)) was lower than the initial pH, for both UP and tap water. The buffering capacity of the tap water results in a less pronounced pH change in tap water compared to UP water. The increased equilibrium pH of the MP500 in OH^- form compared to the Cl^- form of both tap and UP water is explained by the exchange of the OH^- counter ions with alginate in the case of the UP water and a combined effect of ion exchange of alginate and other anions such as sulphate, chloride, or humics in the case of the tap water, in addition to the pH changes caused by Donnan exclusion. The lower pH (5.5) of the UP water in the case of the HCl-conditioned MP500 resin did not significantly affect the protonation of alginate, since this pH is still more than 2 pH units higher than the $pK_{a,1}$ (3.2) of alginate.

Humics removal with MP500 was over 93% for both the OH^- and Cl^- a form of SBA MP500, with ion exchange as the predominant removal mechanism, combined with other mechanisms such as π–π stacking. Both counter ion forms exhibited approximately double the humics removal compared to the removal of alginate, with around 30 and 60 μgC of alginate resp. humics removed by each counter ion form of MP500 from the tap water. Different factors contribute to this relatively low removal of alginate compared to the good removal of humics by the MP500 resin. First, the larger size of alginate leads to size exclusion-based limitations as previously described by Finkbeiner *et al.* (2019) and Purschel *et al.* (2013), who studied MW as a limiting factor for NOM removal by AER.

Similar conclusions were made by Ding and coworkers, who found that the removal of humic acid with a MW above 10 kDa spiked in UP water by MIEX (a magnetic SBA (Cl^-) resin) was about 75% lower compared to the removal of humic acid with MW lower than 10 kDa (Ding *et al.* 2022). Furthermore, Finkbeiner *et al.* (2019) found that both a higher charge density and a higher hydrophobicity of NOM surrogates were associated with improved removal by AER. When comparing the chemical structures and corresponding characteristics of alginate and humics, a higher charge density but a lower hydrophobicity are assigned to alginate. The beneficial effect of the higher charge density of alginate explains the similar removal of alginate in UP and tap water. The relatively low total removal of alginate aligns with the findings of Mergen *et al.* (2008). They used water sources with distinctly different characteristics in terms of, i.e. hydrophobicity and composition as determined by SUVA and resin fractionation, to study their influence on removal by a MIEX (magnetic SBA Cl^-) resin. The DOC removal was the highest (65%) for water with predominantly hydrophobic compounds; however, this water was also characterized by the highest charge density, which strongly influences the removal efficiency as well, as mentioned above. A DOC removal of approximately 30% was obtained for surface water with a high algae content and lower hydrophobicity (Mergen *et al.* 2008). It must be noted that microscopy analysis revealed that most of the algae species in this water belonged to the group of green algae, suggesting that no significant amount of alginate (which is primarily produced by brown algae) was expected. Nonetheless, green algae can secrete hydrophilic anionic polysaccharides that exhibit alginate-like properties (El-Naggar *et al.* 2020).

Finally, the effect of the higher alginate concentration compared to the humics concentration on their removal efficiencies must be considered. This is, e.g., illustrated by Finkbeiner *et al.* 2019 who found that the concentration of a spiked molecule had a major impact on its removal by an SBA resin, with a remarkable decrease in removal from 56 to 9% when the concentration of spiked tannic acid (used as an HS surrogate molecule) was increased from 5 to 670 eq L^{-1}. These results were explained by pore blockage with voluminous compounds such as tannic acid (MW 1.7 kDa), restricting the use of the resin to mainly its outer surface. The higher concentration of alginate could thus also contribute to a relatively lower removal percentage of alginate compared to humics.

WBA MP62 (Cl^-) removed 49% of the spiked alginate and 96% of humics from tap water, while 29% of the alginate in UP water was removed. The difference in alginate removal between the results from the tap and UP water was explained by the lower equilibrium pH. The equilibrium pH (5.9) of the tap water enables removal via ion exchange while the equilibrium pH (3.7) of UP water leads to a higher degree of alginate protonation, resulting in a decreased alginate removal. The interaction between a deprotonated carboxyl group and the basic group of a WBA resin is illustrated in Figure 5. Bolto *et al.* (2002) concluded that WBA resins have a larger affinity for more hydrophilic anions compared to SBA resins, which explains why MP62 removes alginate, which is classified as a hydrophilic anionic polysaccharide, more effectively than MP500.

Dextran spiking experiments

Figure 6 shows an overlay of an HPSEC-TOC chromatogram of tap water and dextran spiked in UP and tap water. The dextran used in this work is defined by the manufacturer as *dextran 40*, indicating an average MW of 40 kDa. This MW corresponds to an elution time (of the peak maximum) of 34.5 min as calculated via the MW calibration with pullulan, which is a polysaccharide with a comparable structure to dextran. The observed peak maximum in the obtained HPSEC-TOC chromatograms at a later elution time indicates a lower average MW. Moreover, dextran elutes over a very wide elution time range (from about 30 to 50 min), corresponding with a wide MW distribution (between about 59.9 and 1.8 kDa as calculated with the pullulan calibration). Due to the wide elution time range, dextran co-elutes with the humics present in the tap water. This impedes a straightforward calculation of the humics concentration based on the HPSEC-TOC chromatogram, especially given the relatively high concentration of dextran compared to the humics concentration. For this reason, the removal of humics was calculated based on the HPSEC-UV chromatograms, since dextran does not absorb UV light at 254 nm and thus does not interfere with the UV measurements.

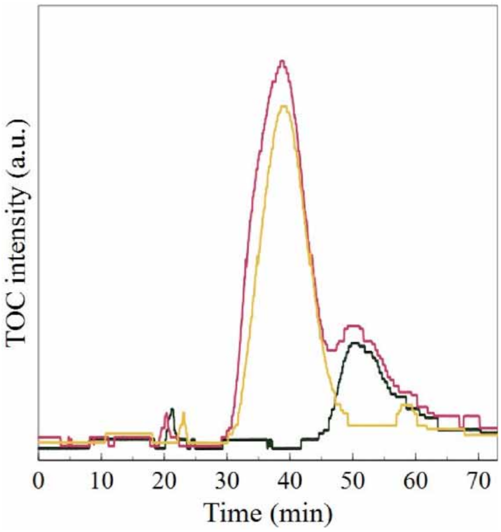


Figure 6 | Overlay of the initial HPSEC-TOC chromatograms of 8 mg L^{-1} dextran spiked in UP water (yellow) tap water (red) and tap water (black).

When comparing the HPSEC-TOC chromatogram of dextran with the one of alginate (see Figure 7), it can be noted that the peak maximum of dextran has a later elution time, indicating a lower hydrodynamic volume. However, as mentioned in Section 3.1, it must be noted that the anionic character of alginate complicates the interpretation of its elution time. The broader elution range of dextran compared to alginate is explained by a wider MW distribution.

Figure 8 shows the initial and equilibrium pH and the removal of dextran and humics in UP and tap water with MP500 (OH^-) and SD-2 (FB). MP500 (OH^-) removed about 95% of the spiked dextran from UP water, while this

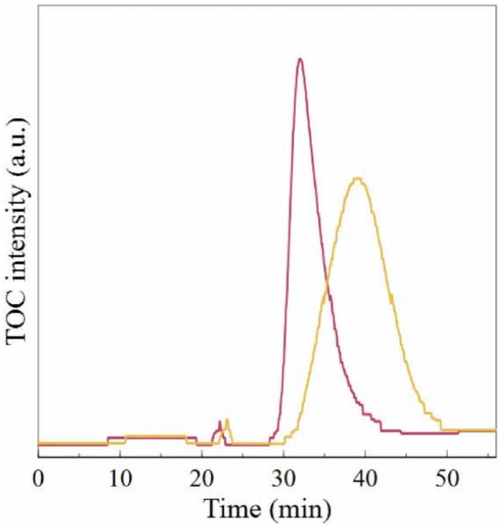


Figure 7 | Overlay of the HPSEC-TOC chromatograms of 8 mg L^{-1} dextran spiked in UP water (yellow) and 8 mg L^{-1} alginate spiked in UP water (red).

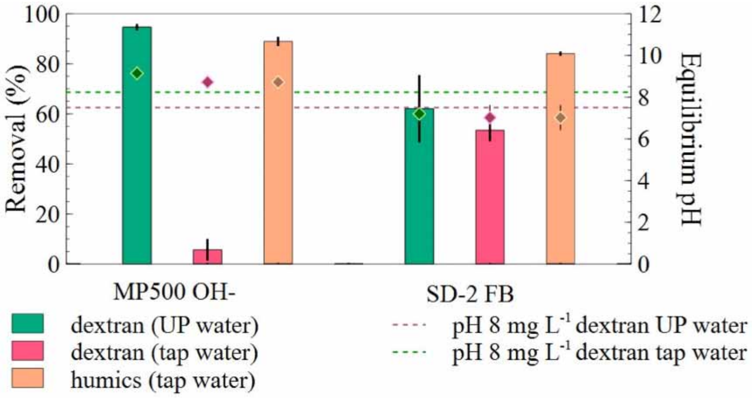


Figure 8 | Removal efficiency (bars) and equilibrium pH (dots) for dextran spiked in UP or tap water and humics from tap water (50 mL spiked water + 2 g L^{-1} NaOH conditioned resin; 22 h, 200 rpm, 25 °C).

resin only achieved the removal of about 6% from tap water. The dextran removal from UP water was explained by H-bonding with the OH^- counter ions (see Figure 9(a)), as described previously by Ijzer *et al.* (2015) and Laforce *et al.* (2022), who linked this mechanism to the removal of glucose and dextran, respectively, from UP water using an SBA resin in its OH^- counter ion form Ijzer *et al.* (2015). This interaction was limited in the

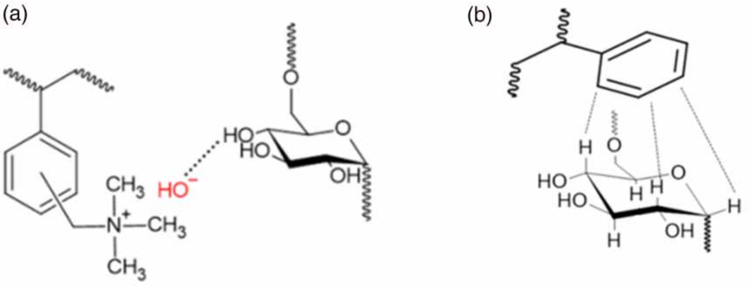


Figure 9 | H-bond formation (indicated by a bold dashed line) as a removal mechanism for molecules having a hydroxyl functionality with an SBA (OH^-) resin (a) and CH–π stacking (thin dashed lines) between the axial positioned H-atoms of a glucose unit and the π-electron system of a benzene ring.

case of tap water due to the exchange of these counter ions with inorganic anions such as sulphate or chloride, or negatively charged organic molecules such as humics from the tap water. The selectivity of SBA resins towards Cl^- and SO_4^{2-} is typically higher than their selectivity towards OH^-, explaining the exchange of the original counter ions in the spiked tap water.

The lightly functionalised WBA resin SD-2 (FB) had a similar removal of humics (84%) compared to the MP500 (OH^-), which was assigned to ion exchange and interactions with the PS matrix. SD-2 removed 62% dextran from UP and 53% from tap water, which was explained by CH–π interactions between the PS resin matrix and the linear polysaccharide (illustrated in Figure 9(b)) (Jimenez-Moreno *et al.* 2015). Previous research showed that WBA MP62 (FB) could not remove any of the spiked dextran from UP water, which indicated that no interactions took place between the WBA functionality and dextran (experiments were conducted with 50 mL of 50 mg L^{-1} dextran solution and 2 g NaOH conditioned WBA MP62; Laforce *et al.* (2022)). In the case of the SD-2, the lower density of functional groups on the matrix facilitates the migration of larger molecules such as dextran to this resin matrix. Therefore, the interactions between these molecules and the resin matrix are enabled. This resin was developed for decolorization in sweetener applications ('DuPont™ AmberLite™ SD-2'). However, to the best of the authors' knowledge, SD-2 has not been previously examined for its ability to remove NOM (surrogates) from water.

When comparing the removal of dextran and alginate with MP500 (OH^-) from UP water, a much higher removal efficiency for dextran is observed. Two factors play key roles in the removal of these NOM surrogates using the SBA resin. First, different mechanisms are involved in their removal. Additionally, the smaller hydrodynamic volume of dextran compared to alginate is beneficial for its removal in UP water by MP500 (OH^-).

The very limited dextran removal from the tap water by this resin indicates it is more favourable to exchange ions from the solution with the counter ions from the resin than the interaction of dextran molecules with the OH^- counter ions of the resin. This can be linked to a higher decrease of Gibbs free energy linked to the exchange of the organic and inorganic anions from the solution (SenGupta 2017).

Humics removal from tap water

The humics removal in the alginate and dextran spiking experiments in tap water (see Figures 4 and 8) with MP500 in both counterion forms was over 90% and showed no significant differences between the experiments or counterionic forms. MP62 achieved a removal of 96% of the humics, at an equilibrium pH of 5.5, which was remarkably lower compared to the equilibrium pH for the MP500 experiments. No clear trends can be found between the equilibrium pH and the humics removal, which is consistent with the results from our previous work (Laforce *et al.* 2022). These findings are in contrast with the results of Ding *et al.* (2022), who studied the effect of an increase in pH of 6–9 by adding NaOH to a mixture of synthetic humic acid (HA) solution and a MIEX resin in batch experiments. They concluded that an increased pH significantly decreased the removal efficiency of the HA. It is, however, important to highlight that the addition of NaOH to the synthetic solution alters the experimental conditions because these extra anions (i.e. OH^-) that are introduced into the solution will compete with HA for the available ion exchange sites. This is in contrast with the pH changes measured in the experiments described in this work. Here, OH^- anions were released from the resin (which was initially in the OH^- form) and replaced by an equivalent amount of anions from the starting solution by IEX.

The lightly functionalised WBA resin SD-2 achieved 84% humics removal from tap water, which is significantly lower than the humics removal of the other WBA (MP62) and SBA (MP500) resins. SD-2 has a lower ion exchange capacity compared to the latter resins (see Table 2), which can explain the lower humics removal by SD-2. Nonetheless, although the capacity of the SD-2 is approximately four to five times less than that of the other tested resins, the observed removal efficiency for humics was only slightly lower. This was explained by the voluminous structure of the humics, suggesting that not all ion exchange sites are accessible in the case of resins with conventional capacities.

When comparing the humics removal from tap water with the results of the spiking experiments with HA in UP water in our previous research (Laforce *et al.* 2022), the removal efficiency for MP62 and MP500 is significantly lower in the latter. One possible explanation for these discrepancies is the chemical properties of the humics from tap water and from this humic acid, as, e.g. indicated by the SUVA values of different water sources in the supplementary information. The benefit of a higher hydrophobicity of NOM for the removal by AER resins was described by, amongst others, Urbanowska & Kabsch-Korbutowicz (2018), who observed that surface water with a relatively higher SUVA was more efficiently removed with WBA and SBA resins than dechlorinated tap water spiked with humic acid and a lower SUVA. They attributed this to the beneficial effects of the higher hydrophobicity and lower average MW of the NOM in the surface water, compared to the spiked tap water (Urbanowska & Kabsch-Korbutowicz 2018). The more efficient removal of the most hydrophobic NOM by the SBA resin is in line with the results of this study. However, while SBA resins are typically found to be more effective than WBA resins for removing hydrophobic, anionic NOM (Cornelissen *et al.* 2008), Urbanowska *et al.* concluded that the WBA resin performed better. This contrary result highlights that comparison between experimental results is challenged by variations in, e.g. concentration of organics, water matrix, resin characteristic, or resin/water ratio.

CONCLUSIONS

Two BP NOM surrogates were spiked in UP and tap water. The removal of these surrogates by different AER was investigated, next to the removal of the humics of NOM present in tap water. The major conclusions of this study are as follows:

- The removal of uncharged BP NOM by use of AER encounters a particular challenge when (an)organic anions are present. This challenge is illustrated by the contrasting outcomes observed in ultrapure (UP) water and tap water, specifically in the context of dextran removal using SBA (OH^-) resins. In UP water, these resins effectively remove dextran, whereas in tap water, the removal efficiency is considerably lower. This discrepancy arises because, in tap water, the OH^- counter ions from the resin are replaced by anions from the surrounding solution. This impedes the removal of uncharged NOM molecules that contain hydroxyl groups through hydrogen bonding with the OH^- counter ions. Therefore, when the removal of uncharged polysaccharides such as dextran is targeted, SBA (OH^-) resins could be promising if used after demineralisation.
- Removal of the anionic polysaccharide alginate, used as a surrogate for negatively charged hydrophilic high MW molecules, was explained by IEX. However, the removal with both WBA and SBA resins was less than 50%, while the humics from tap water were excellent removed (over 90%) by the same mechanism. Size exclusion limitations and higher hydrophilicity of alginate explained the lower alginate removal.
- Lightly functionalised WBA resin SD-2 was introduced, and achieved a dextran removal of over 50 and 60% from the tap and UP water, respectively, by interactions with the styrenic matrix, while these interactions are hindered by the high density of functional groups in the case of conventional high-capacity SBA or WBA IEX resins. SD-2 also removed 84% of the humics from tap water. This illustrates the bifunctional character of lightly functionalised resins, especially for the removal of large molecules, where both interactions with the resin matrix and the functional groups are enabled.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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