

Interactions between organic model compounds and ion exchange resins

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Abstract

Ion exchange (IEX) can successfully remove natural organic matter (NOM) from surface water. However, the removal mechanism is not well understood due to the complexity and variability of NOM in real source waters as well as the influence of multiple parameters on the removal behaviour. For example, this includes the physicochemical properties of the NOM and IEX resin, and the presence of competing anions. Model compounds with a range of physical and chemical characteristics were therefore used to determine the mechanisms of NOM removal by IEX resins. Fifteen model compounds were selected to evaluate the influence of hydrophobicity, size and charge of organic molecules on the removal by ion exchange, both individually and in mixtures. Three different resins, comprising polystyrene and polyacrylic resin of macroporous and gellular structure, showed that charge density (CD) was the most important characteristic that controlled the removal, with CD of $>5 \text{ meq mg}_{\text{DOC}}^{-1}$ resulting in high removal ($\geq 89\%$). Size exclusion of compounds with high MW ($\geq 8 \text{ kDa}$) was evident. The hydrophobicity of the resin and model compound was particularly important for removal of neutral molecules such as resorcinol, which was best removed by the more hydrophobic polystyrene resin. Relationships were identified that provided explanations of the interactions observed between NOM and IEX resin in real waters.

Keywords: ion exchange; model compounds; removal; natural organic matter

46 **Introduction**

47 The removal of natural organic matter (NOM) from surface water is known to be of
48 importance, primarily for reduction of the formation of disinfection by-product (DBPs)
49 in drinking water.¹ Ion exchange (IEX) has been shown to successfully reduce the
50 concentration of NOM, particularly when used in combination with coagulation,
51 specifically in the order of IEX followed by coagulation.²

52 Exchange of NOM onto IEX resin occurs through the release of a counter ion into
53 solution.³ The use of strong base anion resins has been found to remove generally
54 more NOM than weak base anion resins due to the lower number of charged sites
55 available at neutral pH.⁴⁻⁶ However, it has not been clearly shown how the physical
56 structure of the IEX resin influences NOM removal. Some studies suggest that
57 macroporous resins remove NOM more efficiently than gellular resins due to their
58 larger pore diameter.⁴ Others have shown a better performance of gellular resins,
59 attributed to the higher degree of swelling and thus access to exchange sites.⁵ There
60 have also been contrasting results when considering how the chemical structure of a
61 resin influences removal behaviour. Styrene resins have been found to have a higher
62 affinity for compounds with an aromatic structure due to stronger hydrophobic
63 interactions.⁷ However, in other work similar or slightly higher NOM removal was
64 achieved by acrylic resins compared to styrene resins and it was reported that the
65 water content of the resin played an important role in controlling removal.⁴ Similarly,
66 Cornelissen et al.⁵ found no differences in NOM removal between resin types when
67 investigating three acrylic and six styrene resins. On the contrary, higher removal was
68 observed for polyacrylic resins in a study by Humbert et al.⁸. The better performance
69 of this resin was linked to its smaller bead size and the resulting higher easily
70 accessible surface exchange sites.

71 These differences reflect the role that the NOM properties have on removal, where
 72 charge, hydrophobicity and size have all been shown to be important.^{9–11} The most
 73 important removal pathway is the electrostatic attraction between functional groups on
 74 the resin and the negatively charged moieties of NOM molecules. Regarding only
 75 these electrostatic interactions, each exchange is associated with an increase in Gibbs
 76 free energy (ΔG) when a larger ion on the exchanger resin is replaced by a smaller
 77 ion of equivalent valency from the solution, described by equation 1, based on
 78 Coulomb's law:³

$$\Delta G_{el} = -\frac{Ne^2}{4\pi\epsilon_0\epsilon_D}\left(\frac{1}{r_R + r_B} - \frac{1}{r_R + r_A}\right) \quad \text{Equation 1}$$

79 where N is the Avogadro constant, e is the elementary charge, ϵ_0 is the vacuum
 80 permittivity, ϵ_D is the dielectric constant of the ion exchanger, r_R is the charge radius
 81 of the hydrated fixed ion and r_A or r_B that of the counter ions, where A refers to chloride
 82 and B to the ion that is exchanged.

83 The most common anionic groups in NOM are the carboxylate ion with a hydrated
 84 radius of 0.304 nm¹² and the deprotonated hydroxyl ion (no data available for hydrated
 85 radius). During removal, these groups exchange with the chloride ion ($r_{\text{hydrated}} = 0.332$
 86 nm¹³) in a stoichiometrical fashion.¹⁴ A higher number of charged groups relative to a
 87 molecules mass should favour the energy balance and a direct correlation between
 88 CD and bulk NOM removal has been reported previously.¹⁵ However, this is
 89 complicated by other factors such as the molecular weight of organic compounds as
 90 large molecules can experience size exclusion and reduced removal.^{10,16} Several
 91 studies have reported a preferential removal of UV-absorbing DOC by IEX,^{8,17,18} which
 92 indicated that these aromatic compounds are favourably removed by the resin.⁵ The
 93 sorption of the non-polar moiety onto the hydrophobic resin leads to an increase in

entropy which overcompensates the endothermic desolvation, resulting in an overall negative free energy change, making the process favourable.³

The importance and differentiation of these interactions between IEX resin and sorbent is difficult in a diverse mixture such as NOM, where the water matrix can have an effect, such as through complexation with divalent cations and competition with inorganic anions for exchange sites.^{16,21} Accordingly, model compounds can be used to elucidate such interactions as different individual structures can represent the chemical features required for comparison, without the complexity and unknown structure associated with NOM in real water sources. Humic acid, tannic acid and resorcinol have been used as surrogates for hydrophobic NOM, while amino acids and sugars have been used to represent charged hydrophilic and neutral hydrophilic compounds.^{22,23} However, there have been no studies that have considered the combined influence of charge, hydrophobicity and molecular weight when selecting model compounds. This is particularly the case when considering the role of concentration (by mass, molecule and charge), competition and resin property. The aim of this work was to therefore determine the key features of NOM that control removal. This was achieved through investigation of 15 model compounds, spanning a wide spectrum of molecular structure, and three resins of different chemical and physical structure.

Materials and Methods

Model compounds

Model compounds of different hydrophobicity, molecular weight and charge were selected to cover a diversity of physicochemical properties, as well as representing constituents of raw water, including humic substances (humic and fulvic acids), breakdown products (referred to as building blocks), carbohydrates, carboxylic acids

and amino acids (Table 1). Glucose and xylose were selected as model compounds for neutral small aliphatic molecules; glutamic acid as a surrogate for amino acids with one positively and two negatively charged groups. Resorcinol represented a breakdown product of fulvic acids and is an aromatic compound with almost no charged functionality at neutral pH.²⁴ Aromatic compounds with increasing numbers of carboxylic acid group(s) were chosen to compare the impact of the number of charged moieties: benzoic acid, trimesic acid and mellitic acid. Citric acid represented a charged aliphatic low MW acid. Tannic acid was selected as a large hydrophobic compound. Smaller derivatives of this large molecule with a comparable base structure were studied to show differences in molecular weight and hydrophobicity: pentagalloyl glucose (PGG), monogalloyl glucose (MGG) and corilagin. Three different weight-average molecular weights (M_w) between 1.2-15 kDa of the synthetic polymer poly(acrylic acid) sodium salt (PAA) were used to study the influence of size for a charged aliphatic macromolecule.

A solution of 10 mg_{DOC} L⁻¹ was prepared for each model compound. Additionally, solutions of equivalent molar concentration (0.119 mM) and equivalent charge load (0.707 meq L⁻¹) were prepared to compare different concentrations. Equivalence values were chosen to evaluate the influence of equivalent numbers of molecules and charge present in the solution. The working solutions were buffered with 20 mg L⁻¹ NaHCO₃ and adjusted using HCl and NaOH to give a final of pH 7. Mixtures of benzoic acid, resorcinol and tannic acid were prepared at both equivalent mass and molar concentrations (10 mg_{DOC} L⁻¹ and 0.119 mM) to investigate removal kinetics.

Resin preparation and jar tests

Three strong base anion exchange resins were selected based on their application for NOM removal and the differences in their structure (Table S1). The macroporous

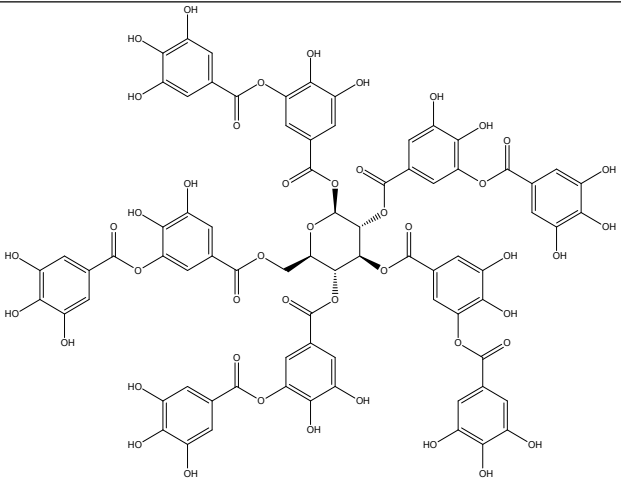
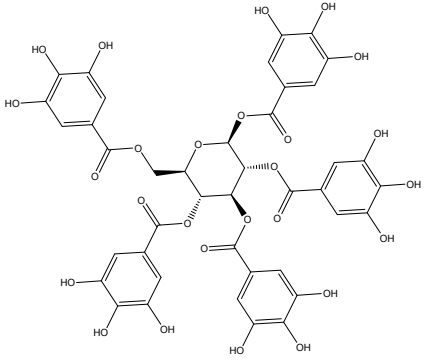
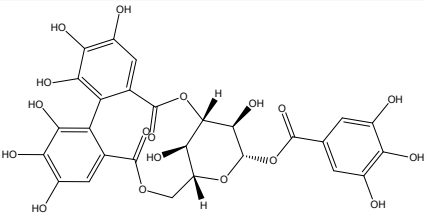
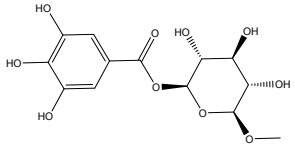
polystyrene Dowex Tan-1 resin had a bead size of 420 to 1200 μm and a capacity of 0.7 eq L^{-1} . The gellular Lewatit S5128 resin had a polyacrylic backbone with a bead size of 400 to 1600 μm and a capacity of 1.25 eq L^{-1} . The third resin was the magnetic macroporous MIEX®Gold resin which was of polyacrylic nature with a bead size of 150-180 μm and a capacity of 0.52 eq L^{-1} .

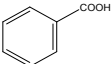
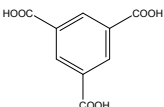
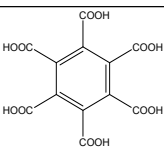
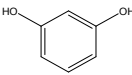
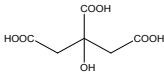
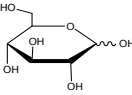
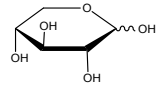
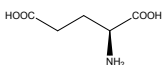
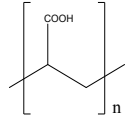
Prior to use, each virgin resin was rinsed using 20 times the resin volume (RV) of deionized water to remove any impurities. The resin was regenerated with sodium chloride solution (20 RV, 100 g L^{-1} NaCl) in stirred suspension for 30 min at 150 rpm. The resin was separated from the brine and rinsed with deionized water (10-20 RV). To remove excess NaCl from the resin pores, the resin was stirred for another 30 min in 20 RV of deionized water at 150 rpm. The required volume of resin was measured in a measuring cylinder then transferred into a 1 L beaker where excess water was removed.

Previous research has shown that the utilisation of resin capacity is low and did not exceed 1.5% of its equivalence capacity during ion exchange of NOM (Finkbeiner et al., 2018, Mergen 2008). This suggests that the resin surface area is more important for NOM removal than the overall capacity for suspended ion exchange systems. Therefore resin concentrations of equivalent surface areas of idealized monodisperse spherical beads were used, normalised to 20 mL L^{-1} of the Lewatit resin, a concentration typical of that used in practice. This resulted in a resin volume of 4 mL L^{-1} for MIEX and 20 mL L^{-1} for Dowex (see supporting information (SI), S.1). The required volume of the conditioned resin was mixed with 500 mL of the model compound solutions in a 1 L glass beaker and stirred with a paddle jar tester. After a contact time of 15 min at a stirring speed of 150 rpm, the resin was allowed to settle. For MIEX resin the settling was assisted by strong neodymium magnets (15 mm

169 radius, pull force 118 N). Each test was carried out in triplicate. Samples were taken
170 after the 15 min experimental time.

171 **Table 1: Chemical structure and physicochemical properties of the model**
172 **compounds.**

Name (constitu- ent)	Structure	Log K _{ow} ^(b)	CD ^(a) (meq mg _{DOC} ⁻¹)	MW (Da)
Tannic acid (humic substance)		6.2	0.56	1701.2
Penta- galloyl- glucose (humic substance/ building block)		3.6	1.08	940.7
Corilagin (building block)		0.1	4.00	636.5
Mono- galloyl- glucose (building block)		-1.3	0.49	332.3

Benzoic acid (arom. CA)		1.87	11.88	122.1
Trimesic acid (arom. CA)		0.5	27.71	210.1
Mellitic acid (arom. CA)		-0.9	41.23	342.2
Resorcinol (neutral arom.)		0.8	0.08	110.1
Citric acid (aliph. CA)		-1.7	41.23	192.1
Glucose (CH)		-2.6	0.00	180.2
Xylose (CH)		-2.5	0.00	150.1
Glutamic acid (AS)		-3.7	33.27	147.1
Poly (acrylic acid) sodium salt	 $n \approx 14, 28, 85, 158$	n.a.	n.a.	n14 =1200 n28 =8000 n85 =15000

173 (a) Charge density calculated based on pKa values estimated with Chemicalize.com
 174 (May 10, 2018), (b) PubChem XlogP3 values, n.a. = not available; CD = charge
 175 density, Log Kow = Octanol-water partition coefficient, MW = molecular weight, aliph
 176 = aliphatic, arom. = aromatic, AS = amino acid, CH = carbohydrates, CA = carboxylic
 177 acid.
 178

Analyses

Prior to analysis, all samples were filtered through a 0.45 μm filter. Dissolved organic carbon (DOC) analysis was carried out using a non-purgable organic carbon method on a total organic carbon (TOC) analyser (TOC-V_{CPH}, Shimadzu). Results were reported as an average of triplicates.

Model compound mixtures were quantified on an Agilent 1200 Series high performance liquid chromatography (HPLC) equipped with a degasser (G1379B, Tokyo, Japan) and ALS autosampler (G1329A, Waldbronn, Germany). A sample volume of 0.1 mL was injected onto a Gemini C6-Phenyl column (5 μm , 110 Å, 150 x 4.6 mm) (further details provided in SI, S.2).

A zetasizer connected to an autotitrator (Malvern Nano Series, Worcestershire, UK) was used to measure the charge load and determine the CD of selected model compound solutions (tannic acid and PAA) using a titration against pol(diallyldimethylammonium chloride) according to an adapted method of Kam and Gregory.²⁵ The theoretical CD was calculated based on the molar concentration of the model compound and its proportion of ionised groups at pH 7 according to their logarithmic dissociation constant (the pKa) estimated by chemicalize.com (May 10, 2018). Determination of the sDBP-FP was carried out as detailed by Finkbeiner et al.¹⁰ In short, the model compound solutions (DOC = 1 mg L⁻¹) were chlorinated with NaOCl (5 mg L⁻¹ of free chlorine) and incubated for 7 days at 25°C. Trihalomethanes (THMs) were quantified with gas chromatograph mass spectrometry (GC-MS) using a headspace method, and haloacetic acids (HAAs) were extracted and derivatised prior to analysis on a GC-MS. The determination of total resin capacity was an adjusted silver nitrate titration method from Harland²⁶ (see SI, S.3).

Results and Discussion

Increased removal at higher charge density

At a model compound DOC concentration of 10 mg L^{-1} , a steep increase in removal with increasing CD was observed for all three resins (Figure 1). For example, PGG had a CD of $1.07 \text{ meq g}_{\text{DOC}}^{-1}$ and was removed by 74-82%. In comparison, benzoic acid with a CD of $11.88 \text{ meq g}_{\text{DOC}}^{-1}$ was removed by 90-93%. This was explained by the higher free energy of the exchange of benzoic acid that occurred due to the increased proportion of charged groups on the molecule. To illustrate, the change in free energy ΔG was $-1.7 \text{ J mg}_{\text{DOC}}$ for benzoic acid, while this was $-0.2 \text{ J mg}_{\text{DOC}}$ for PGG (see S.4 in SI for calculations). Tannic acid, PGG, MGG and corilagin, which share a glucose ring with differing numbers of gallic acid ester groups, followed the same trend of increasing removal with CD. MGG had the lowest CD of the set ($0.49 \text{ meq g}_{\text{DOC}}^{-1}$) and had a removal efficiency of 29%, while corilagin, with a CD of $4.0 \text{ meq g}_{\text{DOC}}^{-1}$, was reduced by 80% when using the Lewatit resin. The higher removal for the higher CD molecule was aligned with an increase in the free energy that favoured ion exchange.

Large improvements in removal were seen when the CD was increased from 0.4 to $4.0 \text{ meq mg}_{\text{DOC}}^{-1}$ while there was little or no change above $11.88 \text{ meq g}_{\text{DOC}}^{-1}$, where $\geq 89\%$ was seen for all resins. For example, the removal for citric acid (CD $41.23 \text{ meq g}_{\text{DOC}}^{-1}$), trimesic acid (CD $27.71 \text{ meq g}_{\text{DOC}}^{-1}$) and benzoic acid ($11.88 \text{ meq g}_{\text{DOC}}^{-1}$) was 93% for the Lewatit resin. The results show that a maximum removal was reached in the CD range between 5 to $10 \text{ meq g}_{\text{DOC}}^{-1}$. Above this threshold, no further increase in removal with higher CD was observed. These results align with observations seen for real surface waters treated by virgin resin that had CDs ranging between 6.2 to $10.5 \text{ meq g}_{\text{DOC}}^{-1}$ resulting in removal between 86-89%.²⁷ Mergen²³

228 showed that CD between 5.5 and 6.5 meq g_{DOC}⁻¹ resulted in removal of 50-65% and a
229 CD of 1.9 meq g_{DOC}⁻¹ resulted in removal of 35%. However, one water source of very
230 low CD (0.3 meq g_{DOC}⁻¹) resulted in 65% removal.

231 The exception to the trend was glutamic acid (CD of 33.27 meq g_{DOC}⁻¹), where removal
232 was less than for other compounds of similarly high CD. This was attributed to the
233 zwitterionic nature of the compound. Repulsive forces, originating from the positive
234 charge carried on the nitrogen atom of the amino acid, resulted in a less favourable
235 exchange. Furthermore, Donnan ion exclusion restricts glutamic acid molecules from
236 entering the resin due to the positive charge on the molecule.³

237 Resorcinol was removed by 9 and 29% by the Lewatit and Dowex resin, whereas
238 MIEX resin showed no considerable removal (2%). At pH 7, the molecule was present
239 almost entirely in the protonated form and of no charge; hence ion exchange would
240 not take place. Hydrophobic effects, and π - π interactions have been proposed as
241 alternative removal mechanisms.¹ Sorption of a hydrophobic compound to the resin
242 results in an increase in entropy and hence leads to a negative ΔG . The Dowex resin
243 had stronger interactions with the resorcinol due to the more hydrophobic and aromatic
244 styrenic resin backbone compared to the polyacrylic resins, explaining the increased
245 removal.

246 The removal of tannic acid was principally driven by its moderate CD (0.56 meq g_{DOC}⁻¹
247 ¹). However, differences in removal were observed for the Lewatit and Dowex resin at
248 57 and 71% respectively. This was explained by the hydrophobic/aromatic interaction
249 of the molecules with the resin backbone. The MIEX resin showed a higher removal
250 of tannic acid (78%) than the other two resins. This was unexpected as the resin has
251 a polyacrylic structure, which is less favourable for removal of compounds of high log

Kow (Table 1). However, this resin has been developed to target high molecular weight organic compounds between 2 and 5 kDa through having reportedly larger pore sizes than other resins used for DOC removal.²⁸ This would allow tannic acid easier access to more exchange sites in the resin. Additionally, the small bead size allows faster kinetics through improved diffusion into the resin. To quantify these effects further, research is required to determine the resin pore size distribution using porosimetry. The neutral uncharged compounds glucose and xylose were not removed by any resin. These compounds possess no charge that could electrostatically interact with the resin. They are also very hydrophilic molecules (log Kow -2.5 to -2.6) and so have very low adsorption potential.

Trimesic, mellitic, glutamic and benzoic acid as well as the sugars glucose and xylose had a negligible sDBP-FP (Figure S1). Tannic acid, PGG and MGG shared a similar sTHM-FP between 33 and 39 mg g_{DOC}⁻¹ and all three had a high HAA-FP of 103, 139 and 197 mg g_{DOC}⁻¹, respectively. Citric acid was equally important for both sHAA- and sTHM-FP with values of 117 and 145 mg g_{DOC}⁻¹. Resorcinol had a low sHAA-FP (31 mg g_{DOC}⁻¹) but a very high sTHM-FP of 1142 mg g_{DOC}⁻¹. There was no correlation between the sDBP-FP and the physicochemical characteristics of the compounds (Figure S2), suggesting that the properties that control their removal by IEX do not relate to sDBP-FP.

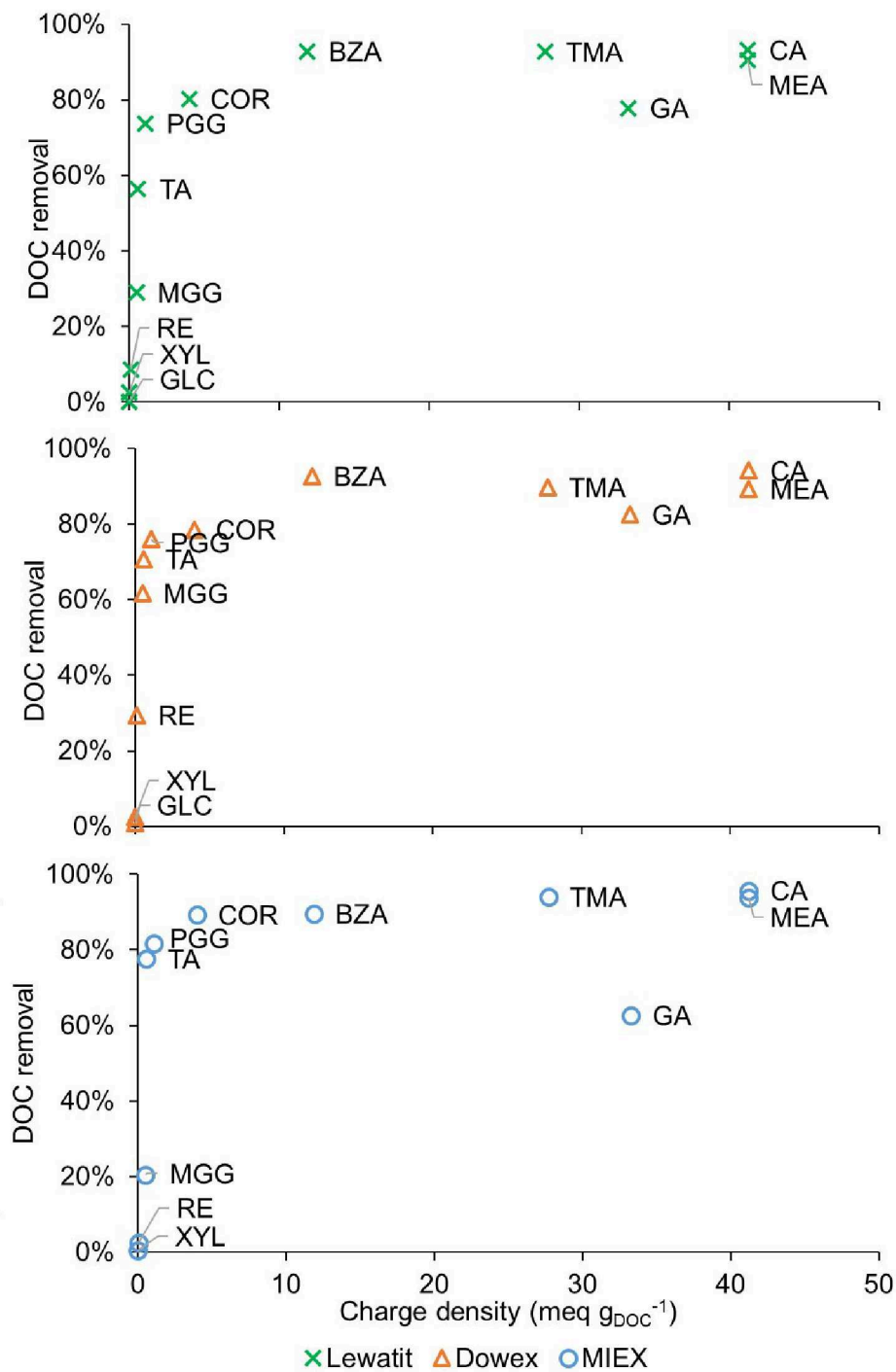


Figure 1: Removal of model compounds as a function of their charge density for a) Lewatit, b) Dowex and c) MIEX resin; BZA = benzoic acid, CA = citric acid, COR = corilagin, GA = glutamic acid, GLC = glucose, MEA = mellitic acid, MGG = monogalloyl glucose, PGG = pentagalloyl glucose, RE = resorcinol, TA = tannic acid, TMA = trimesic acid, XYL = xylose.

Impact of compound concentration on removal

Higher concentrations of organic molecules might influence their removal due to occupation of easy accessible exchange sites, particularly for larger compounds that might block exchange sites. Therefore, solutions of equivalent molar concentration were prepared for eight selected compounds that were well removed by IEX. Additionally, five compounds with CDs $>10 \text{ meq mg}_{\text{DOC}}^{-1}$ were used to prepare solutions of equivalent charge load. Tannic acid was also included here to be representative of a large hydrophobic compound. An increase in charge load (CL) or concentration showed no considerable change in removal for the small molecules ($<350 \text{ Da}$): resorcinol, benzoic acid, trimesic acid, mellitic acid and citric acid (Figure 2). For example, 93% of the benzoic acid was removed at 0.13 and 0.70 meq L^{-1} . Glutamic acid was less well removed with increasing CL, decreasing from 78 to 72% for the Lewatit resin. Pore blockage was not thought to be responsible for this decrease because twice as many of the similar sized benzoic acid molecules were removed (0.64 mM) in comparison to glutamic acid (0.26 mM).

A greater change in removal was observed for larger compounds with increasing charge concentration. For example, when the charge load of PGG (941 Da) was increased from 10 to 60 $\mu\text{eq L}^{-1}$ the removal dropped from 74 to 49% and from 76 to 65% for Lewatit and Dowex resin, respectively. A similar trend was observed for tannic acid (1701 Da): where the Lewatit resin showed a decrease in removal from 56 to 9% across the gradient of 5 to 670 eq L^{-1} . This was congruent with the hypothesis that compounds of high MW were restricted to the outer surface of the resin due to sterically hindered pore diffusion.^{3,29} As a result, reduced removal was observed as the surface area was occupied. The diameter of tannic acid has been estimated to be 3 nm, therefore size exclusion effects were important for the gel type resin with pores

305 of <2-4 nm.^{26,30,31} Also the macroporous resins consist of gel phases that are
306 fragmented by large pores and hence size exclusion can also occur in these resins.^{3,26}

307 ***Molecular weight as a limiting factor***

308 To further study the influence of size while reducing the impact of other
309 physicochemical factors, solutions of PAA of different mass-average molecular weight
310 (M_w) were used. Measurement of PAA solutions resulted in a high CD ranging from
311 21.3 to 24.0 meq g_{DOC}^{-1} . PAA was less well removed with increasing size of the
312 polymer chain for all resins (Figure 3). For a M_w of 1.2 kDa, the concentration of the
313 PAA was reduced by 83, 78% and 81% for Lewatit, Dowex and MIEX resin,
314 respectively. The removal of PAA of 8 kDa was similar when MIEX resin was used
315 (80%). However, the other two resins resulted in removal of 60%, suggesting that size
316 exclusion started to take effect between a M_w of 1.2 and 8 kDa for PAA. While the
317 Lewatit and Dowex showed similar removal efficiencies for low M_w compounds, the gel
318 type resin (Lewatit) had a much lower removal of 28% for the solution containing the
319 largest polymer (15 kDa) compared to the macroporous resin (Dowex) that had a
320 removal of 53%. The macroporous Dowex resin has wider pores, with diameters
321 between 20-100 nm³², which enabled the large molecules to access into the resin.
322 Comparatively, for the microporous Lewatit gel-type resins with pores <2-4 nm access
323 into the resin was restricted and a lower removal observed (Figure 3a and b). Similarly,
324 the macroporous MIEX resin removed 67% of PAA. The improved removal of the large
325 PAA molecule by MIEX was consistent with the high removal of tannic acid and was
326 explained by the large pore size of the resin. While both Dowex and MIEX were
327 macroporous resins, MIEX was able to remove more of the 8 and 15 kDa PAA
328 compounds. This was explained by the higher available accessible resin surface area

for the smaller MIEX in comparison to the Dowex resin when used at equivalent volumetric doses.

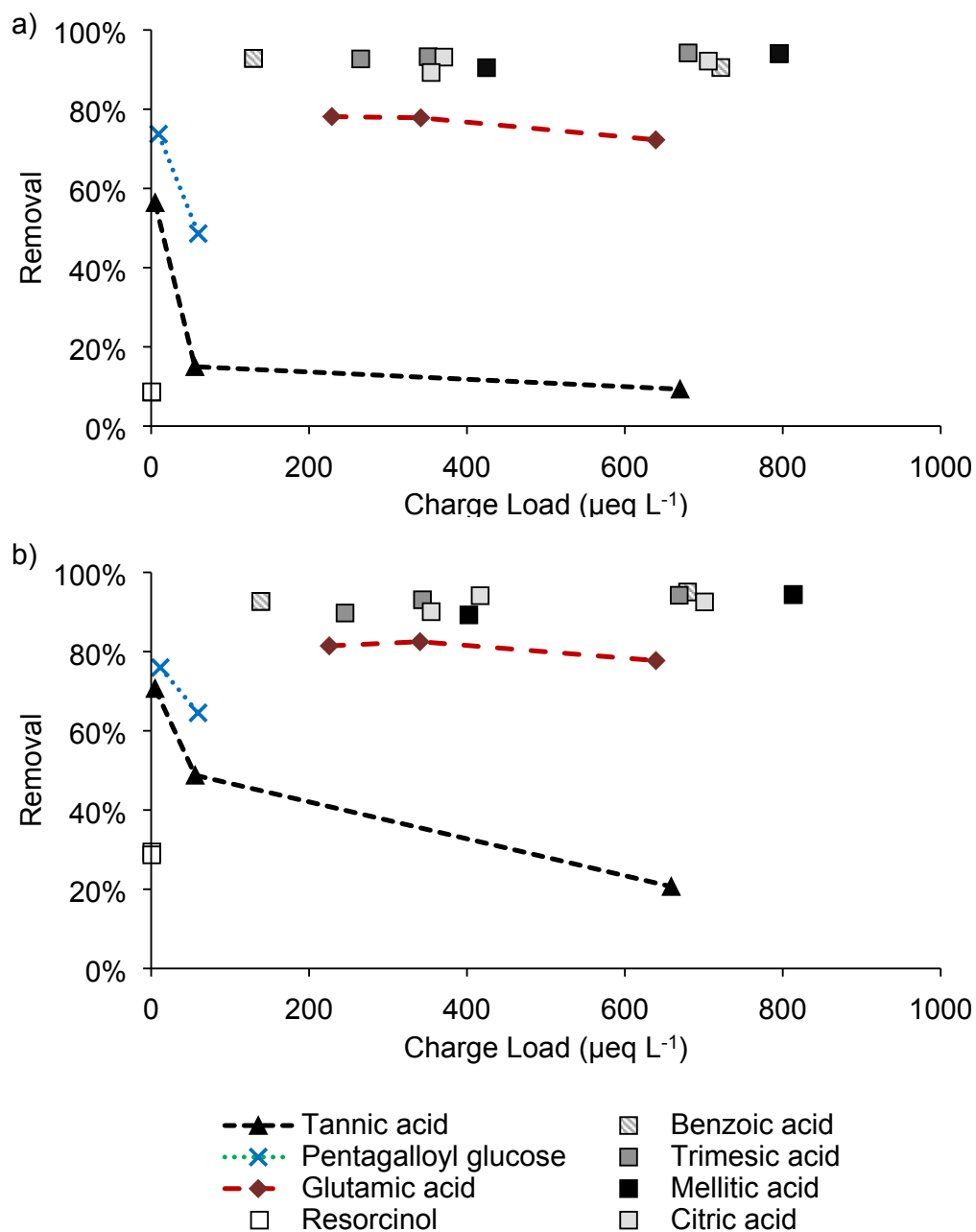


Figure 2. Removal of model compounds at different initial concentrations expressed as charge load for a) Lewatit and b) Dowex resin.

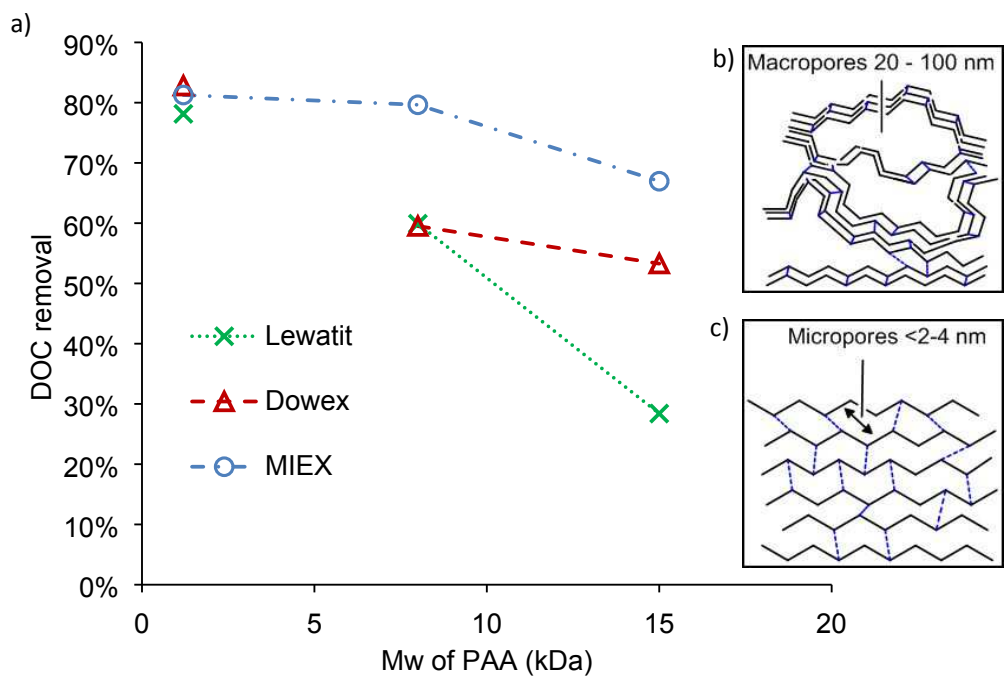


Figure 3: a) Comparison of the removal of PAA (poly(acrylic acid) sodium salt) at different weight-average molecular weight by Lewatit, Dowex and MIEX resin, b) structure of the macroporous resin such as Dowex and MIEX, c) structure of gel-type resin such as Lewatit; (b) and c) were adapted with permission. Copyright 2019 Dardel³²).

Stoichiometric exchange of NOM for chloride

The released chloride concentration was plotted against the theoretically exchanged charge load to evaluate whether a stoichiometric exchange took place (Figure 4). The data points were clustered around the stoichiometric exchange line, with the exception of glutamic and tannic acids. The higher values obtained for tannic acid were explained by an underestimation of the CD calculated from its pKa value (0.56 meq g_{DOC}⁻¹). This was supported by empirical determination of the CD to be 3.2 meq g_{DOC}⁻¹. When this CD value was used, the data points were located much closer to the stoichiometric exchange line (Figure 4).

The CL reduction for glutamic acid was higher than the predicted chloride release. This supported the view that glutamic acid binds to the resin with only one of its carboxyl groups. When the CL reduction for the exchange of glutamic acid was based on only one negatively charged group, this corresponded very well with the released chloride equivalence (circular data points, Figure 4). For all resins, mellitic acid at a set concentration of 0.41 meq L^{-1} resulted in a stoichiometric exchange for all six acidic functional groups. At high initial charge loads (0.8 meq L^{-1}), however, a lower than expected chloride release was observed, which was equivalent to an exchange of between 4 and 5 carboxylate groups. Accordingly, it was considered that not all of the available anionic groups attached to the resin exchange sites as the molecular concentration increased.

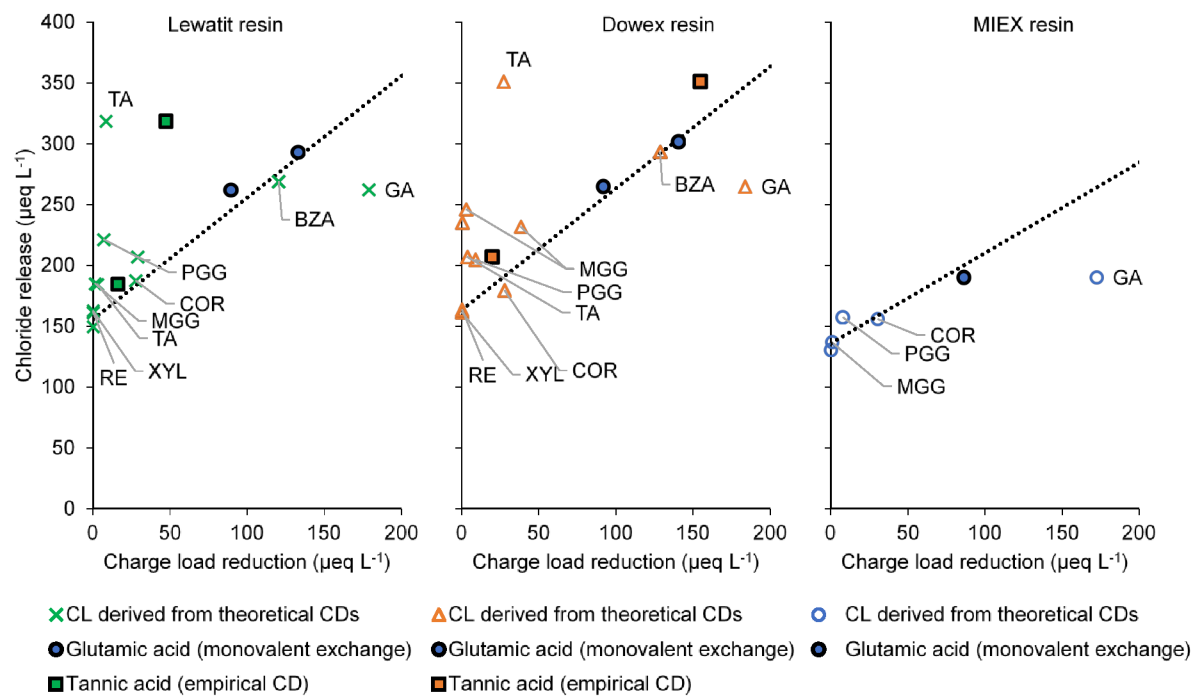
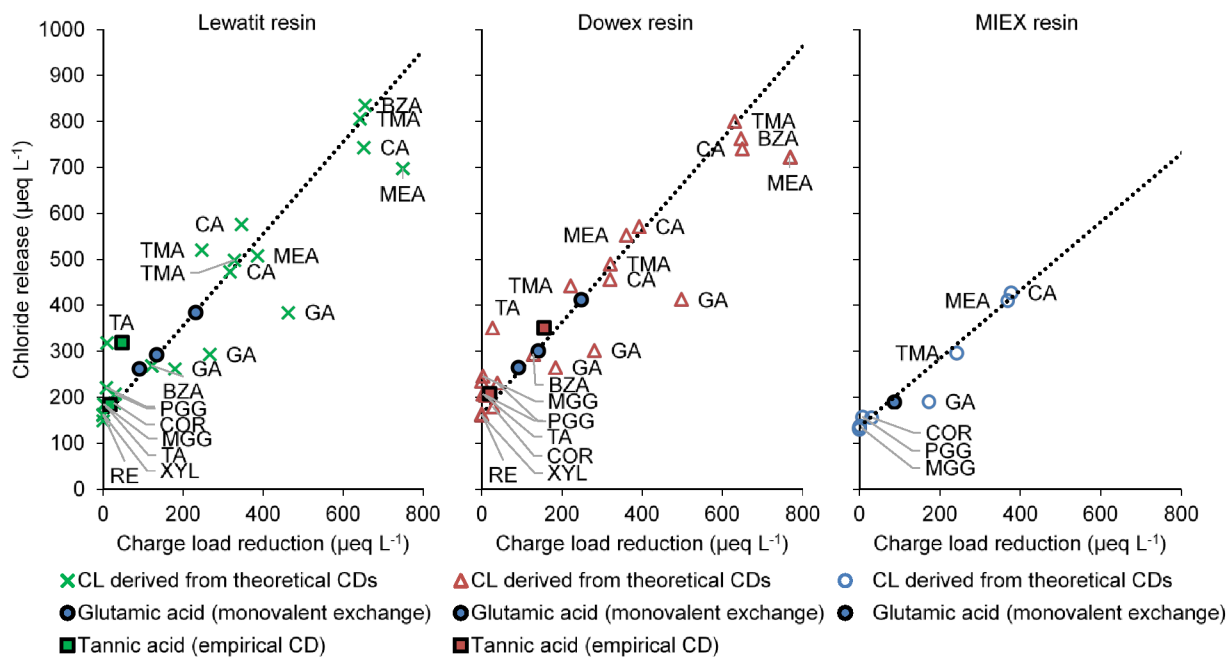


Figure 4: Chloride release as a function of the theoretically removed charge density (CD). The dotted line indicates the stoichiometric exchange of the charged groups of the molecules for chloride. BZA = benzoic acid, CA = citric acid, COR = corilagin, GA = glutamic acid, GLC = glucose, MEA = mellitic acid, MGG = monogalloyl glucose, PGG = pentagalloyl glucose, RE = resorcinol, TA = tannic acid, TMA = trimesic acid, XYL = xylose. *Bottom set of figures shows the same data with re-scaled axes to show detail for the low charge load reductions.*

Competition for exchange sites between contaminants

Where compounds were present at equal DOC concentration (mixture 1), the concentration of benzoic acid showed a rapid decline in the first few minutes and levelled off at concentrations of 0.65, 0.45 and 2 mg L⁻¹ after 15 min for Lewatit, Dowex and MIEX resin, respectively (Figure 5a). The difference between the resins was explained by their chemical structure (styrene vs. acrylic) and the relative occupation of the exchange sites. The same trend was observed for mixture 2, where there was a fixed molar concentration of 0.119 mM for each chemical (Figure 5b). The efficient removal of benzoic acid, even in the presence of a high concentration of tannic acid, indicated that exchange was not inhibited by other components. This was explained by the ability of small aromatic anions to access pores and exchange sites between voluminous anions already exchanged on the resin surface. However, the presence of increased concentrations of tannic acid influences the exchange kinetics. For MIEX resin, the removal kinetics showed a faster rate of removal of benzoic acid in the first few minutes of contact time compared to the other two resins. For instance within 1 min the benzoic acid concentration of mixture 1 was reduced by more than 50% by the MIEX resin, whereas Lewatit and Dowex resin required 2.5 min to achieve the same reduction. The smaller diameter and larger pore sizes of the MIEX resin beads enabled faster intraparticle diffusion and enhanced the ion exchange rate.^{3,26} For benzoic acid, the pseudo first order adsorption rate constant was calculated to be 0.32, 0.37 and 0.55 min⁻¹ for Lewatit, Dowex and MIEX resin in mixture 1 and 0.30, 0.29 and 0.39 min⁻¹ in mixture 2. The higher diffusion rate for Dowex and MIEX resin can be explained by the larger pore size and smaller bead size (MIEX only) which enables faster ion exchange.³⁰ However, at higher tannic acid concentrations (mixture 2) the rate was lower for all resins and can be attributed to the hindrance of benzoic acid

400 removal by the larger organic molecules. When approaching equilibrium, however, the
401 overall removal of benzoic acid was similar for the high and low tannic acid
402 concentration. The benzoic acid removal for MIEX was lower than for the Lewatit and
403 Dowex resin, attributed to the lower frequency of available exchange sites of the MIEX
404 resin. While the total exchange capacity was not exhausted, the relative occupation of
405 the resin was much higher for the MIEX resin (due to its lower charge density)
406 compared to Dowex and Lewatit resin, particularly if removal was limited to the
407 exchange sites near the surface of the resin.

408 The removal of tannic acid by the Dowex resin was shown to be influenced by its initial
409 concentration, but only slightly by the presence of competing compounds. The level of
410 removal was 69 and 46% in mixture 1 and 2 respectively, while in the individual
411 compound solutions it was 71 and 49% (Table S2). Interestingly, there was a higher
412 removal of tannic acid by Lewatit resin in mixture 1 of 64% compared to 56% in the
413 single compound experiment. This was postulated to be due to hydrophobic
414 interactions between the tannic acid and sorbed aromatic benzoic acid molecules on
415 the resin, favouring the removal of tannic acid. The removal of tannic acid by MIEX
416 resin declined when competing compounds were in the solution. Rather than
417 enhancing the removal of tannic acid from the increase in the hydrophobicity of the
418 resin from the sorbed benzoic acid, in this case the competition for exchange sites
419 reduced the sorption of tannic acid to the resin. For mixture 1, the removal was 74%
420 compared to 78% in the single compound experiment. Again, this was ascribed to the
421 overall lower exchange capacity of MIEX resin (0.51 eq L^{-1}) compared to the other two
422 resins ($0.68\text{--}1.15 \text{ eq L}^{-1}$). Resorcinol was removed by up to 8 and 28% for Lewatit and
423 Dowex resin, respectively. The highest removal rate was achieved in the first minute
424 and then declined quickly. The removal of resorcinol in the mixtures was of a similar

magnitude as for the pure compound solutions, and therefore was not considerably impacted by the presence of other compounds. This was explained by the different removal mechanism of this molecule.

With respect to the DBP formation, the increased residual concentration of the high THM forming resorcinol resulted in a considerable increase in the sTHM-FP of mixture 1 (Table S3). . The Dowex resin gave the highest removal of resorcinol and had the smallest increase in sTHM-FP (69%, 741 mg g_{DOC}⁻¹). Less effective removal of resorcinol by Lewatit and MIEX resulted in a higher sTHM-FP. In mixture 2, the concentration of tannic acid was very high and the proportion of resorcinol was relatively small, hence the sTHM-FP of the untreated and treated water was comparatively low (155 and 194-239 mg g_{DOC}⁻¹ respectively). However, the sHAA-FP was reduced by 60-64% for all resins, which was explained by the removal of tannic acid, a high HAA former. The sHAA-FP was higher than expected based on the concentration and individual formation potential (see SI, S.5 for more detail).

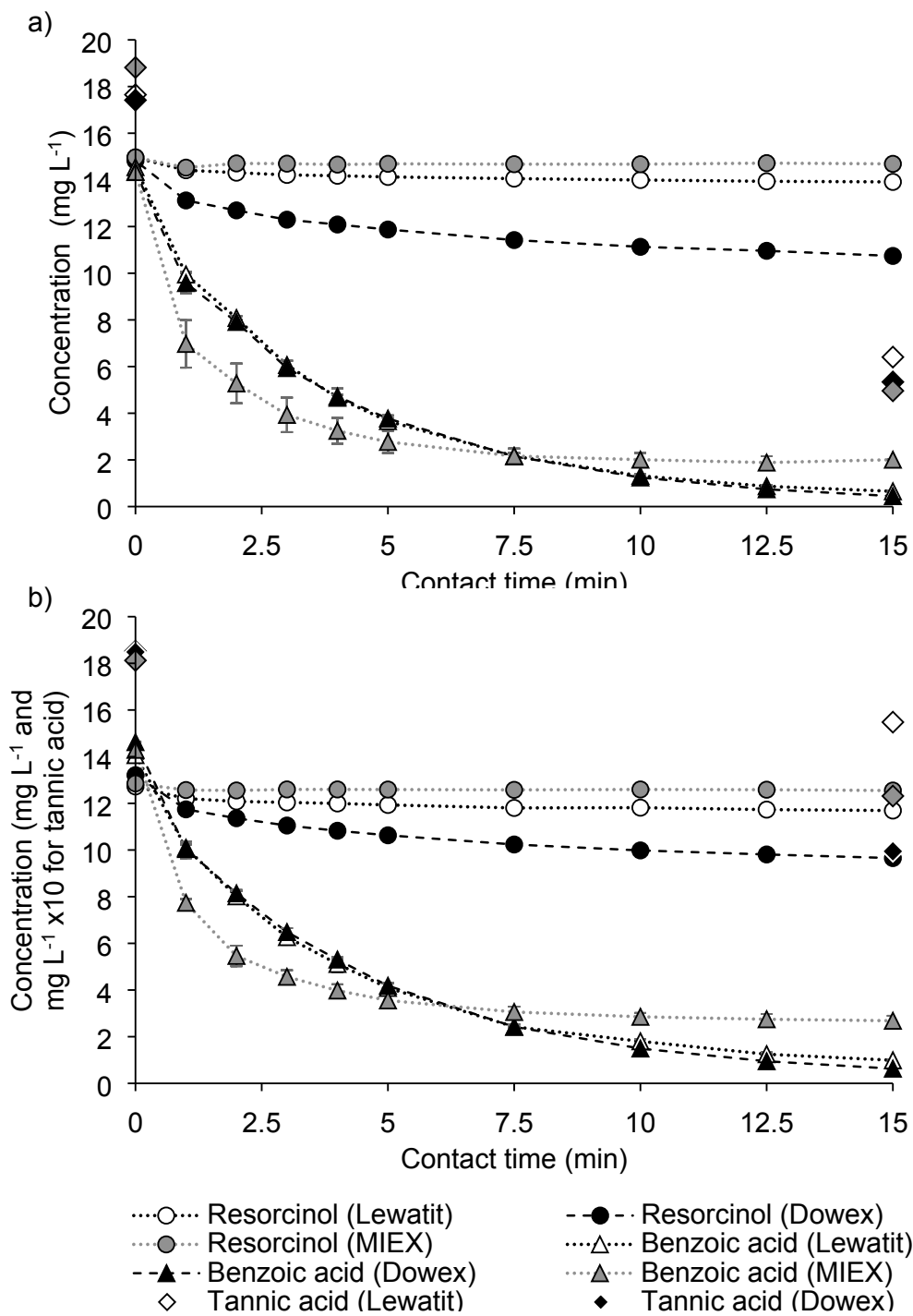


Figure 5: Removal over time for compound mixtures of tannic acid, resorcinol and benzoic acid at a) 10 mg L⁻¹ DOC and b) 0.119 mM of each compound; tannic acid concentration calculated from DOC measurements.

Relating the results to real waters

The influence of charge, hydrophobicity and MW were evaluated using the known structure and physicochemical properties of model compounds. For individual compound experiments, a relationship between CD and DOC removal was seen, with maximum removal observed as the CD approached $10 \text{ meq mg}_{\text{DOC}}^{-1}$. This was consistent with that seen for treatment of real water sources using virgin resin.²⁷ However, while CD is the main driving force behind exchange of NOM onto IEX resins,⁹ when used in multiple cycles, fouling of the resin takes place that limits access of NOM to pores,³³ such that no consistent relationship is seen with DOC removal and CD as hydrophobic interactions and MW contribute to the selectivity.¹⁰

Compounds with multiple charged groups do not necessarily exchange all of their anionic groups, resulting in a higher removal of charge compared to the sites occupied on the resin. This explains the high CL removal efficiency seen for waters of high CD. Furthermore, glutamic acid showed that oppositely charged groups on a molecule inhibited its removal, an aspect that has not been considered in investigations treating real water. Studying individual compounds showed that hydrophobic character noticeably improved selectivity for low CD compounds, especially for resins with a styrene backbone. This was shown by the removal of uncharged hydrophobic molecules. In real water the importance of neutral compounds is very hard to establish as bulk charge density measurements provides only information about the overall charge load. Similarly, when real waters are split into fractions of different hydrophobicity, there is no information provided about the charge of the compounds present. The present work has shown that IEX can provide some removal of hydrophobic compounds such as resorcinol, which can be important contributors to DBPs. While not investigated in the present work, understanding the influence of

471 competing ions in real source water, such as sulphate, nitrate and bromide, on DOC
472 removal should also be assessed as this can influence overall removal and DBP
473 formation and speciation.

474 The model compounds provided further insight into the removal of different sized DOC
475 compounds where it was shown that the removal of molecules such as tannic acid
476 (1.701 kDa) and PGG (0.940 kDa) was lower at elevated concentrations. This
477 supports the view that large compounds block resin pores, consistent with
478 observations seen for real waters for compounds in the 1 kDa fraction.²⁷ The use of
479 model compounds identified that the sDBP-FP and its reduction depended on the
480 composition of the mixture. The ratio of different compounds defined the resulting
481 sHAA- and sTHM-FP, and apparent synergistic effects were observed. These
482 observations help explain why some water types are not effectively treated by IEX and
483 provide explanation as to why IEX treatment results in a reduction of sDBP-FP for real
484 water sources in some cases, while in others no change has been observed.²

485 **Supporting Information.** S.1 Calculation of resin concentration; S.2 Analysis of
486 mixtures; S.3 Determination of resin capacity; S.4 Calculation of free energy; S.5
487 Specific HAA-FP; Table S1 Properties of ion-exchange resins; Table S2 Comparison
488 of tannic acid removal; Table S3 sHAA- and THM-FP of mixture 1 and 2; Figure S1
489 DBP formation for model compounds; Figure S2 DBPs as a function of
490 physicochemical properties.

491 **Acknowledgements**

492 The authors would like to thank Scottish Water for their financial support to conduct
493 this research. The resins used in this study were kindly provided by PWNT, DOW and

494 IXOM. The authors thank Adel Abrar from Phenomenex for his support in developing
495 a method for the HPLC analysis.

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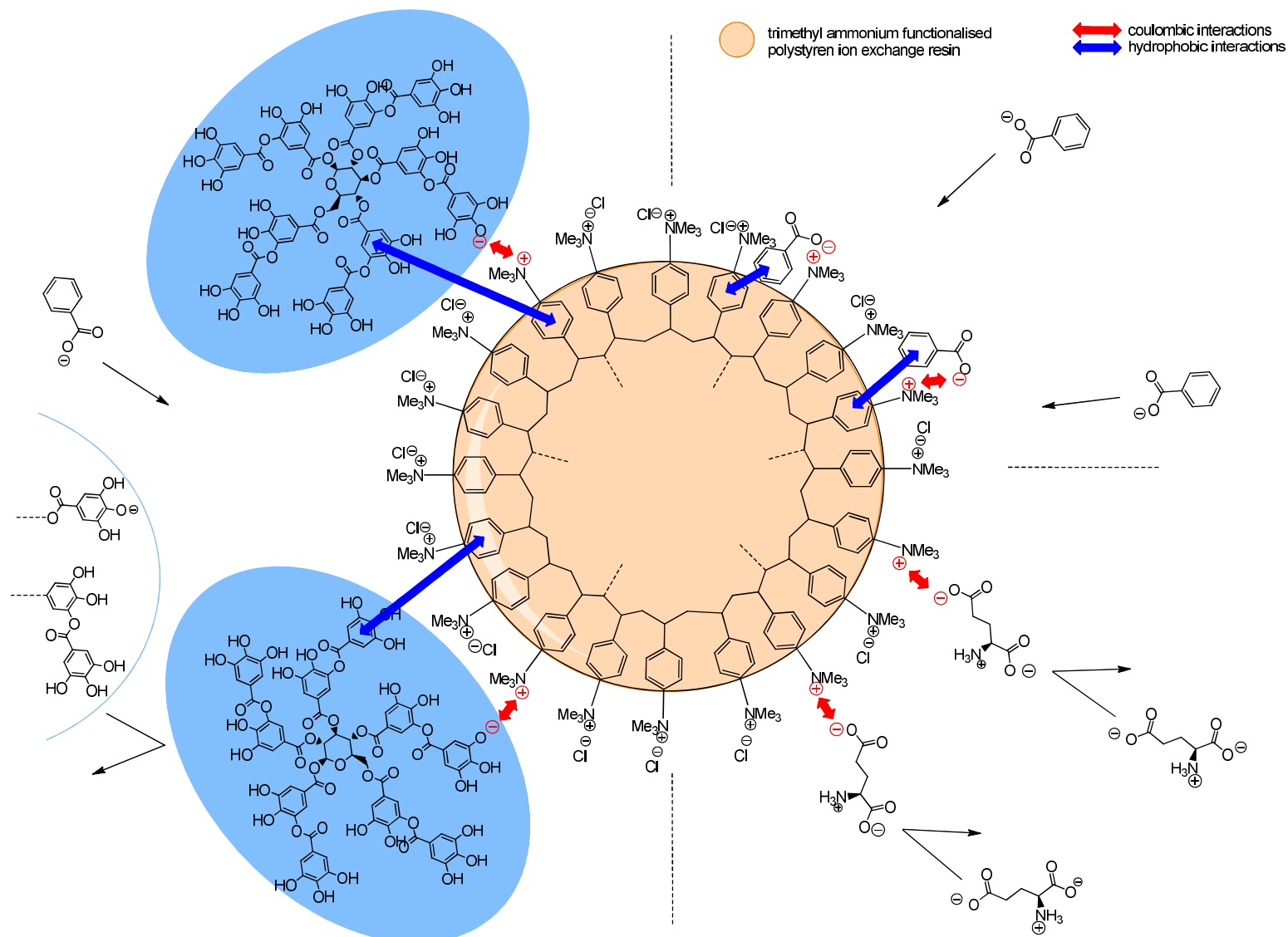
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Interactions between organic model compounds and ion exchange resins

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2019-07-22

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Finkbeiner P, Moore G, Tseka T, et al., (2019) Interactions between organic model compounds and ion exchange resins. Environmental Science and Technology, Volume 53, Issue 16, July 2019, pp. 9734-9743

<https://doi.org/10.1021/acs.est.9b02139>

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