



Uptake of NOM fractions by anion-exchange resins in demineralization plants

Madlen Pürschel^{a,*}, Eckhard Worch^b, Volker Ender^a

^a*Faculty of Mathematics/Natural Sciences, University of Applied Sciences Zittau/Görlitz, Theodor-Körner-Allee 16, Zittau 02763, Germany*

Tel. +049 3583 61 1707; Fax: +049 3583 61 1740; email: m.puerschel@hszg.de

^b*Institute of Water Chemistry, Dresden University of Technology, Dresden 01062, Germany*

Received 3 April 2013; Accepted 4 July 2013

ABSTRACT

The elimination of natural organic matter (NOM) is an important objective of water treatment in demineralization plants of power stations, because NOM is considered to be a corrosion risk factor in the steam water cycle. The aim of this study was to compare the performance of different anion-exchange resins (AERs) relating to their NOM fractions removal in demineralization treatment (input water with acidic pH after cation exchange). NOM removal was assessed using the dissolved organic carbon (DOC) measurement and the liquid chromatography–organic carbon detection (LC–OCD) method. At acidic pH, weak base AERs with their higher total volume capacities (TVCs) showed also higher NOM uptakes in comparison with strong base AERs. Further, the macroporous polystyrene weak base AER MP64 was found to be the most effective AER for the removal of problematic NOM leakage fractions (hydrophobic organic carbon (HOC), biopolymers, low-molecular-weight (LMW) neutrals) before the breakthrough point of the stronger adsorbed anions.

Keywords: Natural organic matter (NOM); Demineralization; Anion-exchange resin (AER); Adsorption; Water treatment

1. Introduction

In all raw water sources for demineralized water, natural organic matter (NOM) occurs, which is a complex mixture of organic materials such as biopolymers (proteins, amino sugars, polypeptides), humic substances (humic and fulvic acids), building blocks (hydrolysates of humics), low-molecular-weight (LMW) neutrals and LMW acids (e.g. alcohols, ketones, aldehydes, amino acids).

In the demineralization plants of power stations, much effort has been made to remove NOM, since it is considered to be a corrosion risk factor in the steam water cycle because of the possible decomposition to LMW acids and carbon dioxide [1,2]. Therefore, a limit of 100 ppb total organic carbon (TOC) is recommended for these waters [3]. In case of relative low NOM concentrations in the raw water, this limit can be achieved by using anion exchange resins (AERs) in conventional demineralization plants [2]. In cases, where the raw water is contaminated with higher concentrations of NOM and increased fraction of biopolymers, the combination of anion exchange with reverse osmosis [4],

*Corresponding author.

ultrafiltration [5] or activated carbon [6,7] was shown to be effective. However, if a conventional demineralisation plant supplies water with slightly above 100 ppb TOC, there are following options: (i) to extend the present plant with a cost intensive reverse osmosis or another method, (ii) to do nothing with the risk of corrosion or (iii) to optimise the use of AERs (e.g. resin structure and functional groups). In this work, we focus on the third way.

NOM removal by AERs under acidic pH conditions (pH 2.0–2.5) has been observed in several investigations [2,5,7]. The acidic pH is relevant because the feed water of an anion exchanger in demineralization plants is the acidic effluent of the upstream cation exchanger. The NOM uptake capacities are mostly influenced by matrix material, porosity, and functional groups of the AERs as well as by the input water composition [8]. Studies by Huber and Gluschke [9] have shown that NOM with large molecular size or/and low charge densities cannot be removed by AERs at acidic pH in satisfying quantities. Following the liquid chromatography–organic carbon detection (LC–OCD) classification after Huber and Frimmel [10], these problematic NOM fractions are particulate organic carbon (POC), hydrophobic organic carbon (HOC), biopolymers and neutrals. Ender et al. [11] have revealed that about 40% of the remaining TOC in the makeup water of power stations comes from the POC and HOC fractions, compared with 16% in the input water. In the remaining chromatographically detectable organic carbon, 80% are biopolymers and neutrals.

As a consequence, the uptake performance of different AERs in regard to problematic NOM fraction was investigated at acidic pH with 2-naphthol (model substance for LMW neutrals) [12] and different types of starch (model substances for biopolymers) [13,14]. For 2-naphthol, highest uptake capacities were estimated onto macroporous (MP) polystyrene weak and medium base AERs. Furthermore, investigations with different types of starch indicate that size-exclusion dominantly influence the NOM removal by AERs. It was found that the smaller the size of the NOM molecules and the higher the water content of the AERs, the higher the uptake is. Thus, for the removal of biopolymers and POC with large molecular size, polyacrylic resins with high water content could be a better option.

In the present study, the NOM uptake capacities were investigated with “real” water obtained from a demineralization plant of a power station. Besides the overall NOM capacities of the AERs, the NOM uptake before the anion breakthrough is of special interest, since it reveals the quality of the demineralized water. Therefore, the main aim of this study was to evaluate

the NOM (fraction) uptake performances of different AERs at acidic pH before anion breakthrough to avoid leakage of TOC in the demineralized water. For this objective, eight different anion exchangers were investigated in view of their NOM (fraction) and anion uptake. The AERs differ in their polymer composition (polystyrene versus polyacrylic matrix) and charged functional groups (tertiary versus quaternary amines). The different resin properties were useful for understanding the interactions between NOM and the AERs as well as the mechanisms which determine the removal efficiency. The NOM uptakes were estimated from breakthrough curves (BTCs) obtained by laboratory-scale filter experiments. NOM was measured as dissolved organic carbon (DOC). Additionally, for some samples, the LC–OCD method was applied to investigate the behavior of the different NOM fractions.

2. Materials and methods

2.1. Anionic-exchange resins

The NOM uptake performances of eight fresh AERs were studied at acidic pH (Table 1). The AERs were selected in order to cover a broad range in matrix material and functional groups. All AERs were used in the hydroxide form, which is the application form in demineralization plants of power stations after cation exchange. AERs characteristics were obtained from product data sheets of the manufacturers. Total volume capacities (TVCs) of the AERs, which is the amount of functional groups present on the resin materials per volume, were calculated from experimental sulfate BTCs (up to $c/c_0=1$) by the application of the integral mass balance equation like described for instance by Worch [15]. Sulfate BTCs were obtained from fixed-bed studies with 0.01 M H_2SO_4 (obtained from KMF). The effluents were analyzed by titration measurements (titrant: 0.02 M NaOH; indicator: bromothymol blue (both from Merck); detection limit: 0.0015 M). The evaluation of the TVCs based on three column experiments for each resin (relative standard deviation at about 2.6%).

The cleaning procedure of the resins was optimized to minimize organic leachables from the AERs in column experiments. Best results were found for the following procedure applied for 100 mL resin: washing with millipore water (conductivity $<1 \mu S/cm$, pH 5.8 and DOC $<50 \mu g/L$), threefold shaking (1 h) with 500 mL 0.1 M NaOH, sequenced treatment in a soxhlet reactor first with 250 mL methanol and after that with 250 mL acetonitril (each for 24 h), washing with millipore water and rinsing with 400 mL 1 M

Table 1
Properties of the selected anion exchangers

Parameters	Resin type		
	IRA96 ^a	AP246 ^b	IRA900 ^a
Material Structure	Polystyrene MP	Polyacrylic MP	Polystyrene MP
Functional group	Tertiary ammonium	Tertiary/quaternary ammonium, type I	Quaternary ammonium, type I
Water content (%)	57–63	60–65	58–64
TVC – pH 2 (mol _{eq} /L)	1.46 ± 0.07	1.44 ± 0.08	0.81 ± 0.11
ρ_B (g/L)	670	710	700
ρ_P (g/L)	1,050	1,080	1,065
ε_B (-)	0.362	0.343	0.343
d_P (mm)	0.73	0.47	0.735
	MP64 ^d	MP500 ^d	MP600 ^d
Material Structure	Polystyrene MP	Polystyrene MP	Polystyrene MP
Functional group	Tertiary/quaternary ammonium, type I	Quaternary ammonium, type I	Quaternary ammonium, type II
Water content (%)	61–66	62–67	45–50
TVC – pH 2 (mol _{eq} /L)	1.37 ± 0.06	0.86 ± 0.03	1.14 ± 0.02
ρ_B (g/L)	620	660	680
ρ_P (g/L)	1,040	1,070	1,100
ε_B (-)	0.404	0.383	0.382
d_P (mm)	0.59	0.64	0.62
			VPOC1071 ^d
Material Structure			Polyacrylic GEL
Functional group			Quaternary ammonium, type I
Water content (%)			66–72
TVC – pH 2 (mol _{eq} /L)			1.05 ± 0.09
ρ_B (g/L)			700
ρ_P (g/L)			1,080
ε_B (-)			0.352
d_P (mm)			0.725

Notes: ^aRohm and Haas, France S.A.S., Chauny Cedex, France; ^bBayer AG, Leverkusen, Germany; ^cPurolite, Bala Cynwyd, USA; ^dLewatit, Lanxess GmbH, Leverkusen, Germany; MP = macroporous; TVC = total volume capacity = anion exchange capacity (median value ± measurement uncertainty after student t-distribution); ρ_B = bed density; ρ_P = particle density; ε_B = bed porosity; d_P = particle diameter.

Table 2
DOC in water samples after batch experiment with untreated and soxhlet-treated resins

Parameters	Resin type								
	MP strong base AERs, type I			MP strong base AER, type II	Gel-type strong base AER, type I	Weak and medium base AERs			
	IRA900	MP500	A860	MP600	VPOC1071	IRA96	MP64	AP246	
Experiment with untreated resins									
DOC (ppb)	245.8	122.9	29.3	163.9	174.9	630.3	79.2	n.a.	
Experiment with soxhlet-treated resins									
DOC (ppb)	76.2	14.4	5.7	n. d.	74.6	352.3	60.0	n.a.	

Notes: MP = macroporous; AERs = anion-exchange resins; DOC = dissolved organic carbon; n.a. = not analyzed; not detectable.

NaOH, 300 mL 1.4 M HCl and again twice with 400 mL 1 M NaOH (each step with 4 BV/h), and final washing with millipore water. NaOH were obtained from VWR and HCl, methanol and acetonitril from Merck. All AERs were stored in millipore water.

The success of the cleaning procedure by soxhlet extraction was tested subsequently in batch experiments. For this, 50 mg untreated as well as soxhlet-treated resins were shaken for 24 h with 100 mL millipore water (200 rpm). The amount of organic leachables (analyzed as DOC using a TOC analyzer multi N/C UV HS from Analytik Jena AG) in the decanted water solutions was measured. The DOC concentrations in the water samples for the experiments with untreated as well as soxhlet-treated resins are given in Table 2.

As can be seen in Table 2, considerably lower DOC concentrations were found with soxhlet-treated resins. This is valid for all investigated AERs.

2.2. Test water

The test water was obtained from the demineralization plant of the power station Boxberg, Germany (Vattenfall Europe Generation AG). The raw water, a mixture from the rivers Schwarze Schöps and Spree, was treated by coagulation ($\text{Al}_2(\text{SO}_4)_3$ and coagulant aid on polyacrylamide basis), neutralization/precipitation ($\text{Ca}(\text{OH})_2$) and filtration (multilayer filter containing anthracite and silica sand). This pretreatment procedure is generally able to reduce the DOC concentration significantly depending on the NOM content and composition of the input water [2,5].

Thereafter, the water was treated with cation exchanger, trickling degasser, anion exchanger and mixed-bed exchanger in the demineralization plant. The TOC content in the test water was measured after each treatment unit with the aim to quantify the impact of each step in regard to TOC removal. The

results are shown in Fig. 1. The TOC measurements were done in the DOC Labor Dr Huber (Karlsruhe, Germany).

It can be seen from Fig. 1 that the anion-exchange process has the main impact on the TOC removal in demineralization plants. Thus, optimizing the use of AERs has the highest potential to increase the TOC uptake in water treatment processes.

For this reason, the test water was collected after passing the cation exchanger. The water was stored at 5°C to prevent bacterial growth. The composition of the NOM fractions was analyzed by DOC Labor Dr Huber (Karlsruhe, Germany); pH, conductivity and ion concentration values were obtained from the laboratory of the power plant Boxberg (details given in the following chapter). Chemical properties of the test water are listed in Table 3.

Table 3 shows that the DOC concentration of the water after cation exchange was relatively high (3.96 mg/L), which reveals the requirement for further NOM removal.

The pH of the test water was very acidic (pH 2.24). It is proposed that NOM has a low charge den-

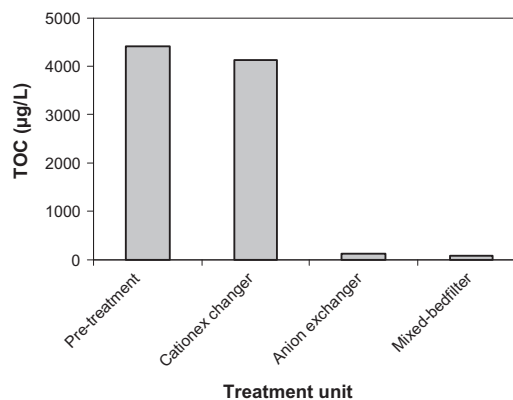


Fig. 1. TOC contents of the test water after each treatment unit.

Table 3
Characterization of test water after cation exchange

Parameters	Test water
DOC ($\mu\text{g/L}$)	3,956
HOC ($\mu\text{g/L}$)	426
Biopolymers ($\mu\text{g/L}$)	29
Humic substances ($\mu\text{g/L}$)	1,875
Building blocks ($\mu\text{g/L}$)	883
LMW neutrals ($\mu\text{g/L}$)	686
LMW acids ($\mu\text{g/L}$)	56
pH (–)	2.24
Conductivity ($\mu\text{S/cm}$)	1,635
Ca^{2+} (mg/L)	0.006
Mg^{2+} (mg/L)	n.d.
Na^+ (mg/L)	1.060
K^+ (mg/L)	n.d.
Cl^- (mg/L)	28.6
NO_3^- (mg/L)	15.9
SO_4^{2-} (mg/L)	163
HCO_3^- (mg/L)	n.a.
SiO_2 (mg/L)	9.75

Notes: DOC = dissolved organic carbon; HOC = hydrophobic organic carbon; LMW = low-molecular weight; n.d. = not detectable; n.a. = not analyzed.

sity under acidic pH condition due to protonation of their acidic functional groups [8,16]. Hence, NOM uptake from acidic water onto AERs occurs most likely by weak van der Waals interactions [17]. We also estimated high sulfate content in the test water. In contrast to NOM adsorption, the uptake of sulfate ions by AERs is supposed to be due to stronger ionic interactions. One consequence could be that stronger adsorbable sulfate ions compete with weaker adsorbable NOM for polar anion exchange sites and thereby limit NOM removal [18].

2.3. Analyses

The concentration of NOM was measured as DOC using a TOC analyzer multi N/C UV HS (Analytik Jena AG), based on wet chemical oxidation with an oxidation agent (sodium peroxodisulfate from Carl Roth) and ultraviolet radiation with subsequent infrared detection of the formed CO_2 (detection limit at $50 \mu\text{g/L}$). Each sample was measured twice. The two-sample standard deviation was about 1.4%.

Advanced NOM characterization was carried out using LC–OCD following the method of Huber and Frimmel [10]. The analyzer was equipped with a column ($2 \times 25 \text{ cm}$) filled with Toyopearl Gel HW 50S, which allows a separation of DOC into fractions depending on their molecular size (biopolymers,

humic substances, building blocks, LMW neutrals and LMW acids). The oxidation was performed in a thin-film reactor with subsequent infrared detection. For the determination of the amount of each fraction, polyethylene glycol standards were used. The calculated fraction that remained on the chromatography column is the HOC. LC–OCD measurements were carried out by DOC Labor Dr Huber (Karlsruhe, Germany).

The pH was measured by a WTW pH 340-meter using a Sentix 41-electrode, the conductivity by a WTW cond. 340-meter using a TetraCon 325-electrode. Ion concentration and SiO_2 determinations were performed in the analytical laboratory of the power plant Boxberg. Cation concentrations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES) analysis (Perkin Elmer Optima 3300 DV), whereas anion concentrations (Cl^- , NO_3^- , SO_4^{2-}) were measured by ion chromatography analysis (Dionex ICS-1100). The SiO_2 content in the water samples was determined by photometric measurements (Dr Lange Lasa 100).

2.4. Column experiments

Fixed-bed adsorption runs were carried out in glass columns with inside diameter of 1.0 cm. The column was filled with 5 mL of freshly regenerated and rinsed AER. Water after cation exchange (pH 2.24) was fed to the top of the column at a constant flow rate of 83 mL/h (equal to 1.06 m/h) regulated by a constant-speed tubing pump (Ismatec, Germany). The column effluent samples were collected regularly once per hour and analyzed by DOC and conductivity measurements. The overall error of a single measuring point in BTCs was about 5.5%. LC–OCD studies were additionally applied for effluent samples at 25 and 100 bed volumes (BV; input solution volume related to reactor volume) to control the water quality before the breakthrough point. NOM uptake capacities were calculated from experimental BTCs (up to $c/c_0 = 0.5$) by application of the integral mass balance equation.

3. Results and discussion

For the test water, the measured DOC and conductivity BTCs for the eight investigated AERs are shown in Fig. 2.

Fig. 2 shows that NOM (measured as DOC) as well as anions (indirectly measured by conductivity) were adsorbed in a good manner by all resins up to at least 100 BV ($c/c_0 < 0.3$). Between about 125 and 300 BV the weaker adsorbed NOM was displaced by the stronger adsorbed anion component (mainly sulfate). As a result

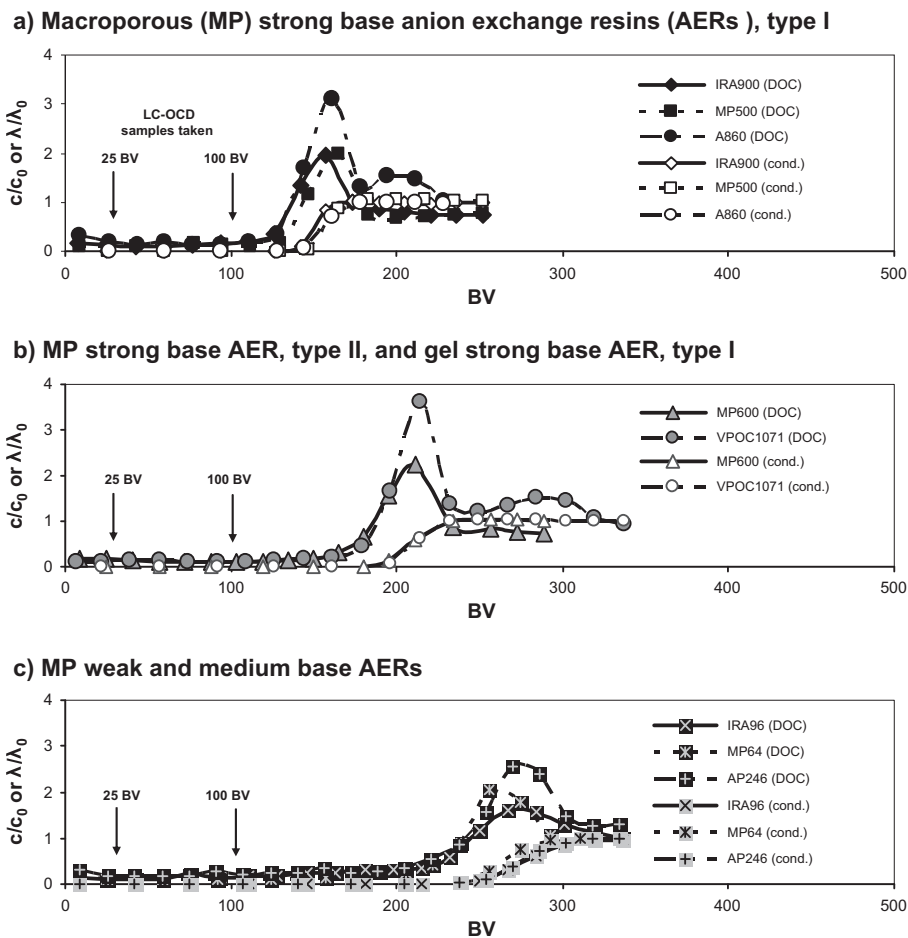


Fig. 2. Reduced NOM concentration (DOC) and reduced conductivity (cond.) in dependence of the treated bed volumes (BV; input solution volume related to reactor volume) for eight different AERs (pH 2.24).

of this competition and displacement, a concentration overshoot ($c/c_0 > 1$) can be observed for the weaker adsorbable NOM. The adsorption capacity of the resins was exhausted at about 175–300 BV, when $c/c_0 = 1$ for all components (NOM and anions).

From the BTC data shown in Fig. 2, the lowest NOM uptakes (0.56–0.74 mg/g DOC) were estimated for the MP strong base AERs of type I (IRA900; MP500; A860), which also have the lowest TVCs (see also Table 1). Medium NOM capacities (0.89–0.91 mg/g DOC) were found for the MP strong base AER of type II (MP600) and the gel-type strong base AER (VPOC1071) with intermediate TVCs. The highest NOM uptakes (0.84–1.26 mg/g DOC) were determined for the MP weak and medium base AERs (IRA96, MP64 and AP246), which also exhibits the highest TVCs. These results confirm that competitive uptake between weaker adsorbable NOM components and stronger adsorbable anions (mainly sulfate ions) occurs.

The matrix material and the structure of the AERs have also an impact on the NOM uptake. In

the present work, we found that MP polystyrene resins have NOM capacities which are to some extent higher than those of MP polyacrylic resins, although their TVCs are nearly equal (IRA900 and MP500 versus A860 as well as IRA96 and MP64 versus AP246). The lower capacities for MP polyacrylic resins could be due to a low amount of nonadsorbable NOM components.

Since polystyrene resins are more hydrophobic, they display an improved affinity for aromatic compounds than resins based on a polyacrylic structure [19,20]. In contrast, AERs with polyacrylic structure tend to be more hydrophilic and they have a more open structure and higher water content [8]. Thus, they exhibit enforced removal of larger molecules, like biopolymers and fulvic acids, than the polystyrene ones [8,14]. In the present study, we found higher NOM capacities for MP polystyrene resins than for MP polyacrylic resins. Thus, it can be concluded that the hydrophobic interactions have a significant higher impact on the NOM uptake from the acidic test water

Table 4
DOC in effluent samples at 25 and 100 BV throughput for eight different anion exchangers

Parameters	Resin type								
	MP strong base AERs, type I			MP strong base AER, type II	Gel-type strong base AER, type I	Weak and medium base AERs			
	IRA900	MP500	A860	MP600	VPOC1071	IRA96	MP64	AP246	
DOC (at 25 BV; in ppb)	227	155	268	283	159	265	138	292	
DOC (at 100 BV; in ppb)	376	292	377	289	256	260	240	332	

onto AERs than size-exclusion limitations. This could be expected, since the DOC concentration of the biopolymer fraction was significantly lower in the test water with 29 µg/L than the DOC concentrations for HOC and LMW neutral fractions with 426 µg/L and 686 µg/L, respectively.

Due to their more hydrophobic character, MP polystyrene strong base AERs of type I should be more successful in the NOM uptake than those of type II with their ethanolic content in the quaternary ammonium group. However, the MP polystyrene strong base AER of type II (MP600) has a significant higher TVC, so that the overall NOM capacity is increased in comparison with those of the MP polystyrene strong base AERs of type I (IRA900, MP500, A860). The TVC of the MP600 resin is comparable with that of VPOC1071, which is a gel-type polyacrylic strong base AER. The last one has a slightly higher NOM uptake despite its polyacrylic structure. This result is in accordance with results of Tan et al. [21] and Cornelissen et al. [22], who also found higher NOM removal with gel-type resins. This could be attributed to a higher swelling capacity of the gel-type resins in water. On the contrary, Bolto et al. [23] reported that MP resins remove more NOM, since NOM components can diffuse easier within the MP structure. The effect of MP versus gel-type structure on the adsorption of NOM should be investigated in more detail in a further study.

In demineralization plants, the loading of the AER is generally stopped at a certain BV or at a point, where the conductivity or silicic acid concentration increase. In this study, it could be shown that the increase in the NOM content (measured as DOC) is a better alternative as switch-off criteria. Loading stop at the point of DOC increase avoids breakthrough of anions as well as of weaker adsorbed NOM components, which are considered as serious corrosion risk factor in the steam water cycle.

Furthermore, the NOM slip in the demineralized water up to the NOM breakthrough is of special interest. For that reason, the DOC in the effluent samples was measured at about 25 and 100 BV throughput

(before NOM and inorganic anion breakthrough occur, see Fig. 2) for the eight investigated AERs. The results are presented in Table 4.

It is shown in Table 4 that the DOC leakage increases in the effluent samples at 25 BV according to: MP64 < MP500 < VPOC1071 < IRA900 < IRA96 < A860 < MP600 < AP246. The order in the effluent samples at 100 BV is slightly different with MP64 < VPOC1071 < IRA96 < MP600 < MP500 < AP246 < IRA900 < A860. This might be explained with the beginning TVC exhaustion of the strong base AERs.

In conclusion, lower DOC escapes in the demineralised water were found for MP polystyrene AERs (e.g. MP64 and MP500) and gel-type polyacrylic AER (VPOC1071) than for MP polyacrylic AERs (AP246 and A860). All estimated DOC concentrations at 25 and 100 BV were above the recommended 100 ppb [3]. However, for the AERs with lower DOC in the effluent (MP64, MP500, VPOC1071), there is an opportunity that the adjacent mixed-bed filter enables to meet this limit.

Additionally, LC–OCD analysis was performed to determine the extent to which different fractions of NOM were removed by the AERs (Fig. 3).

The results in Fig. 3(a) and (b) show that humic substances (humic and fulvic acids) were removed up to 100% at 25 and 100 BV throughput. At acidic pH, NOM components have a low charge density due to protonation of their acidic functional groups [8,16]. Hence, the removal of humic substances at pH 2.24 occurs most likely by van der Waals interactions between NOM components and the anionic resins [17] as well as by precipitation. Humic acid precipitation on the resin material at pH values lower than pH 3.5 is a known effect and for example shown in the study by Ender et al. [13].

Further, it can be seen that building blocks and LMW acids were also preferentially removed by AERs at pH 2.24, whose uptake could also be based on van der Waals interactions. In the effluent samples at 100 BV, the removal of building blocks and LMW acids on the strong base AERs decreased to some extent, probably due to the beginning of the AERs exhaustion (Fig. 3(b)).

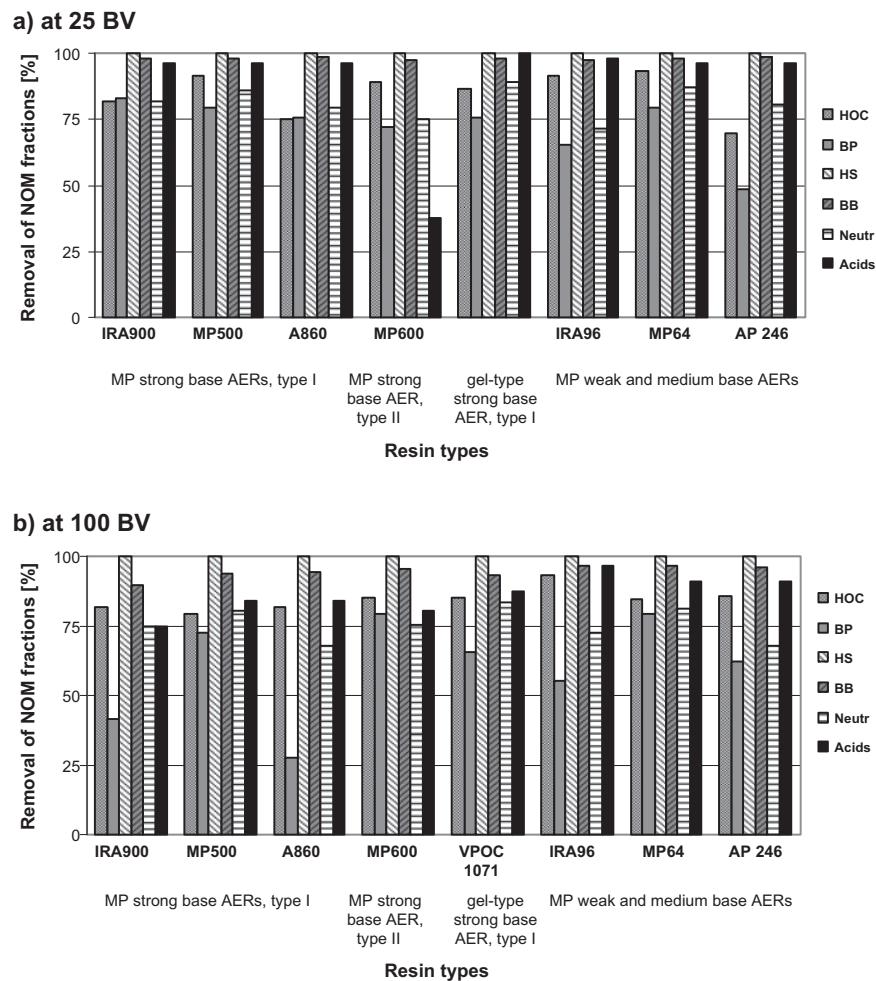


Fig. 3. Removal of NOM fractions as determined by LC–OCD in the effluent samples at 25 and 100 BV throughput for eight different AERs (pH 2.24; HOC=hydrophobic organic carbon; BP=biopolymers; HS=humic substances; BB=building blocks; Neutr=low-molecular-weight (LMW) neutrals; acids=LMW acids).

The uptake of the HOC, biopolymer and LMW neutral fractions on the AERs was less efficient. Due to weaker interactions with the resin material, these fractions are in general firstly displaced and found in the AER filtrates (see Fig. 3(a) and (b)).

Summing up, the most effective AER types for the removal of problematic NOM fractions were found to be MP500, IRA96, and MP64 for the HOC fraction, IRA900, MP500, and MP64 for the biopolymer fraction and MP500, VPOC1071, and MP64 for the LMW neutral fraction. The MP polystyrene medium base AER MP64 has a relative high TVC and performs the best overall NOM fraction elimination within the examined resins. In addition, the gel-type polyacrylic strong base AER VPOC1071 was found to be the best working strong base AER regarding NOM uptake in our study. In the case that MP polystyrene weak and strong base AERs have to be combined in the technical process, then the

IRA96 and MP500 are the best tested choices to optimise NOM adsorption.

4. Conclusions

Under acidic pH conditions, the NOM sorption occurs predominately by weaker van der Waals interactions, whereas the anion uptake is based on stronger ionic interactions. These different behaviors result in displacement effects and leads to concentration overshoots ($c/c_0 > 1$) of the weaker adsorbed NOM components. As a consequence, it was found that the higher the TVC of the AER, the higher the overall NOM uptake is.

Further, the NOM leakage up to the switch off signal caused by conductivity or the more sensitive DOC concentration increase is very important. It was found that humic substances were completely removed by all

resins surely attributable to precipitation processes and van der Waals interactions between NOM components and the anionic resins. Also, each AER showed high uptake affinities for building blocks and LMW acids, which could also be removed by van der Waals interactions. Lower uptakes were found for HOC, biopolymer and neutral fractions, due to weaker interactions with the resin material. As a main result of this study, the most effective AER types for the removal of problematic NOM fractions were found to be MP500, IRA96, and MP64 for the HOC fraction, IRA900, MP500, and MP64 for the biopolymer fraction and MP500, VPOC1071, and MP64 for the LMW neutral fraction.

In sum, at acidic pH condition, it was found that the MP polystyrene medium base AER MP64 performs the best overall NOM fraction removal within the examined resins. Further, the gel-type polyacrylic strong base AER VPOC1071 is the best tested strong base AER concerning NOM uptake. If MP polystyrene weak and base strong base AERs have to be integrated in the technical process, then the IRA96 and MP500 are the best tested alternatives to optimise NOM adsorption.

In future studies, the influence of resin structure (MP or gel-type), resin size and water content should be investigated in more detail. Additionally, regeneration experiments should be applied for all AERs under neutral and acidic pH conditions to study their specific fouling character.

Acknowledgments

The authors thank Dr Torsten Lehmann for helpful support in water sampling and analysis in the power plant Boxberg and stud. chem. Thomas Petrick for extensive experimental work in the laboratory. We are grateful to Vattenfall PowerConsult GmbH and Vattenfall Europe Generation AG for financial support of this work. Further, we thank Rohm and Haas France S.A.S., Bayer AG, Lanxess GmbH and Purolite for providing us with the anion exchange resins.

References

- [1] R. Svoboda, J. Denk, C. Maggi, Influence of carbon dioxide on corrosion in steam turbines, *Power Plant Chem.* 5 (2003) 581–586.
- [2] S.A. Huber, The behaviour of natural organic matter in water treatment and the water/steam cycle: Deeper insights, *Power Plant Chem.* 8 (2006) 105–116.
- [3] VGB standard, Guidelines for Feed Water, Boiler Water and Steam Quality for Power Plants/Industrial Plants, 3rd ed., instruction sheet VGB-S-010-T-00;2011–12.DE. VGB Power-Tech Service GmbH, Essen, 2011, p. 116.
- [4] H. Schley, A. Markert, Reverse osmosis as part of the makeup water treatment in the Lippendorf Power Station, in: Proceedings of the Zittau Power Plant Symposium “Application of ion exchange and membrane techniques to makeup boiler water treatment in power plants”, October, Oybin, 2004, pp. 16–17.
- [5] P. Hübner, Organics removal in water treatment plants, *Power Plant Chem.* 13 (2011) 426–435.
- [6] T. Schönfelder, A. Lutat, Chemistry of steam water cycles of the Rostock Power Station with special viewing to organic ingredients, in: Proceedings of the Zittau Power Plant Chemistry Symposium “TOC in steam water cycles”, Scientific Reports of the University of Applied Sciences Zittau/Görlitz 67, Zittau, 2000, pp. 26–43.
- [7] T. Luukkonen, R. Hukkanen, J. Pellinen, J. Rämö, U. Lasse, Reduction of organic carbon in demineralized make-up water with activated carbon, *Power Plant Chem.* 14 (2012) 112–119.
- [8] T.H. Boyer, P.C. Singer, Stoichiometry of removal of natural organic matter by ion exchange, *Environ. Sci. Technol.* 42 (2008) 608–613.
- [9] S.A. Huber, M. Gluschke, Chromatographic characterization of TOC in process water treatment, *Ultrapure Water* 3 (1998) 48–52.
- [10] S.A. Huber, F.H. Frimmel, Size-exclusion chromatography with organic carbon detection (LC-OCD): A fast and reliable method for the characterization of hydrophilic organic matter in natural waters, *Vom Wasser* 86 (1996) 277–290.
- [11] V. Ender, B. Kettner, T. Schumann, S. Hajdamowicz, The influence of temperature on the removal of organics from natural waters by ion exchange—Laboratory and pilot plant experiments, *Power Plant Chem.* 8 (2006) 117–125.
- [12] M. Pürschel, E. Worch, V. Ender, Uptake of the low-molecular-weight neutrals NOM fraction by different anion exchange resins—Equilibrium data and modelling of breakthrough curves, in: Proceedings of the 3rd International Conference “Interaction of Organics and Organic Plant Cycle Treatment Chemicals with Water, Steam, and Materials”, Heidelberg, March, 2012, pp. 21–23.
- [13] V. Ender, T. Schumann, S. Sachs, G. Bernhard, On the uptake mechanisms of organics from natural water—Investigations with strong and weak base ion exchangers and their corresponding copolymers, *Power Plant Chem.* 8 (2006) 541–549.
- [14] M. Pürschel, S. Sachs, G. Bernhard, V. Ender, Uptake of multi-disperse starch by anion exchangers, *J. Phys. Sci. Appl.* 3 (2013).
- [15] E. Worch, Adsorption Technology in Water Treatment, Fundamentals, Processes and Modeling, De Gruyter, Berlin, 2012.
- [16] J.D. Ritchie, E.M. Perdue, Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter, *Geochim. Cosmochim. Acta* 67 (2003) 85–96.
- [17] J.-P. Croué, D. Violleau, C. Bodaire, B. Legube, Removal of hydrophobic and hydrophilic constituents by anion exchange resin, *Water Sci. Technol.* 40 (1999) 207–214.
- [18] C.T. Anderson, W.J. Maier, Trace organics removal by anion exchange resins, *J. Am. Water Works Assn.* 71 (1979) 278–283.
- [19] H. Humbert, H. Gallard, H. Suty, J.-P. Croué, Performance of selected anion exchange resins for the treatment of a high DOC content surface water, *Water Res.* 39 (2005) 1699–1708.
- [20] M. Gottlieb, The reversible removal of naturally occurring organics using resins regenerated with sodium chloride, *Ultrapure Water* 11 (1996) 53–58.
- [21] Y. Tan, J.E. Kilduff, M. Kitis, T. Karanfil, Dissolved organic matter removal and disinfection by product formation control using ion exchange, *Desalination* 176 (2005) 189–200.
- [22] E.R. Cornelissen, N. Moreau, W.G. Siegers, A.J. Abrahamse, L.C. Rietveld, A. Grefte, M. Dignum, G. Amy, L.P. Wessels, Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions, *Water Res.* 42 (2008) 413–423.
- [23] B. Bolto, D. Dixon, R. Eldridge, S. King, K. Linge, Removal of natural organic matter by ion exchange, *Water Res.* 36 (2002) 5057–5065.