Reduction of Organic Carbon in Demineralized Make-up Water with Activated Carbon Filtration

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ABSTRACT

Organic compounds in the water-steam cycle are an emerging issue at recovery boiler plants. Decomposition products of organic compounds, mainly organic acids with low molecular weight and carbon dioxide, are often related to corrosion. Removal of organics from recovery boiler make-up water with activated carbon (AC) was investigated both in pilot and full scale experiments. AC was used in a novel way to remove organic compounds from demineralized water. AC is conventionally used before demineralization, but when implemented later in the process the lifetime of AC can be extended. Total organic carbon (TOC), conductivity, silica concentration and composition of organic compounds were monitored during the experiments. Results show that AC filtration is a suitable technology for TOC removal from demineralized water. A TOC reduction of 38–70 % was achieved. Mixed-bed ion exchange after the AC filters proved to be necessary to remove conductivity, which was increased in the AC bed.

INTRODUCTION

Recovery boilers are an essential part of pulp mills using sulphate process. They have two separate functions: recovery of pulping chemicals and steam production by combustion of waste materials (black liquor) [1]. Recovery boilers which supply steam to many separate processes, resulting in incomplete recovery and losses of condensate, are often integrated as part of a large factory complex. Therefore large quantities of make-up water are needed. Make-up water requirements can be up to 50–70 $kg \cdot s^{-1}$ and even relatively very small amounts of impurities (e.g. organic compounds) present in the make-up water can have dramatic negative effects on the operation of a water-steam cycle. Mathews [2] lists organic compounds in the cycle as one of the most important challenges in water-steam cycle chemistry.

Organic compounds in the make-up water originate from raw water (mainly natural organic matter, NOM), organic internal water treatment chemicals and impurities (lubricants, oils, degraded ion exchange resins etc.) [3–5]. Organic compounds decompose at high temperatures and pressures of the water-steam cycle. End products are low molecular weight organic acids (mainly formic and acetic acid), ammonia and carbon dioxide [4]. Organic acids and carbon dioxide are related to corrosion in a water-steam cycle although there is some controversy on their relevance [6,7]. One of the reasons for the aggressive corrosive nature of the decomposition products is the absence of a balancing counter cation for formed anions (e.g. formiate and acetate). Anionic decomposition products also mask cation conductivity measurements, preventing the detection of the potentially more corrosive chloride and sulphate [3,4]. Organic compounds can also contain harmful contaminants such as chloride and release them in decomposition processes [8].

The recommended limit for total organic carbon (TOC) in the make-up water is usually 100–200 $\mu g \cdot L^{-1}$, depending on the operating temperature and pressure of the boiler [9,10]. There is a need to operate recovery boilers as well as other steam electric power plants at higher temperatures and pressures in order to produce electricity that is more energy efficient. The higher the temperature and the pressure, the greater the decomposition of organic compounds that occurs. Therefore TOC removal efficiency has a link to energy efficiency.

Over 90 % of organic compounds are typically removed with the combination of conventional chemical water treatment and demineralization processes. There are however electrically neutral fractions (e.g. polysaccharides, proteins and low molecular weight compounds) present in surface waters that remain in the produced make-up water [8]. As a result, conventional demineralization performed by ion exchange cannot remove these fractions effectively [8]. Currently, there are a number of processes that can produce very low TOC level water: reverse osmosis (RO), electrodeionization (EDI) and short wavelength

UV radiation [11–13]. However, the production of high volumes of demineralized water can be expensive with these techniques.

In boiler water treatment granular activated carbon (AC) filters are conventionally used as a last step before demineralization whilst powdered AC can also be used after the coagulation phase in a water treatment process [8,14]. AC can effectively remove organic compounds (especially high molecular weight species) by adsorption and by operating as a bioreactor. The biological mechanism requires certain levels of nutrients in the water before accumulation of microorganisms is sufficient. However the question of microorganisms contaminating treated water often arises if the water to be treated is very pure.

In this study demineralized water was treated further with an AC filter followed by a mixed-bed ion exchanger (MB). There was also a subsequent AC filter after the MB unit. TOC reductions were monitored for 11 months and 3 months in pilot scale filters (Figure 1) and full scale AC filters (Figure 2), respectively. Our goal was to evaluate whether AC can be used to treat demineralized water in order to reduce the residual TOC level without posing a risk of contaminating the water with, for example, microorganisms. We also hypothesized that the operation time of an AC filter could be very long due to low levels of TOC in the influent water.

EXPERIMENTAL

Experimental Setup

The first part of the experimental work was to determine the TOC removal efficiency of an existing water treatment process (plant A) and to compare that with two other water treatment processes (plants B and C) using the same raw water source (the Oulu River). Process schemes of the studied processes are shown in Figures 3–5.

Two pilot scale AC filters and a mixed-bed ion exchange (MB) unit were installed inside a stream at plant A as shown in Figure 1. The volumes of the filters were 34 L (AC2), 18 L (MB) and 18 L (AC1). The ACs used in the experiments were acid washed low ash content CPG-LF 12X40 (AC1 filter) and AQUACARB 608C 12X40 (AC2 filter). The AC beds were wetted for about 24 h and then rinsed continuously until online conductivity measurements settled at a constant value. The MB resin used in the experiment was Purolite MB 400, and the flow at each filter was maintained constant at 1.5 $\text{L} \cdot \text{min}^{-1}$ with rotameters. Samples for TOC analysis and side stream for online conductivity measurements were taken after each unit. The AC filters were monitored over the period 18.12.2010 – 12.10.2011.

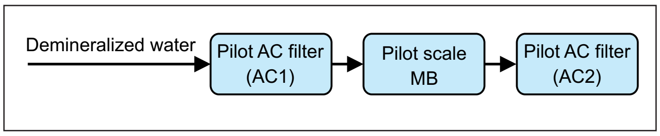

Figure 1:
Testing scheme of pilot scale activated carbon filters (AC1 and AC2) and mixed-bed ion exchanger (MB). Demineralized water was taken from phase 6 in Figure 3.

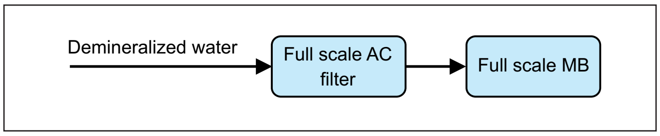

Figure 2:
Testing scheme of full scale activated carbon filter (AC) and mixed-bed ion exchanger (MB). Demineralized water was taken from phase 6 in Figure 3.

A full scale AC filter (old anion exchanger tank, volume 3.86 m^3) was also studied at plant A, whose testing scheme is shown in Figure 2. The AC used in the full scale experiment was AQUACARB 608C 12X40. Once again the AC bed (volume 2.2 m^3) was wetted and rinsed in the same way as the pilot scale AC filters. Flow to the AC filter was approximately 8 $\text{L} \cdot \text{sec}^{-1}$. Conductivity and silica were monitored online and TOC samples were taken before and after the AC filter and MB unit. The full scale AC filter was monitored over the period 23.3.2011 – 6.7.2011.

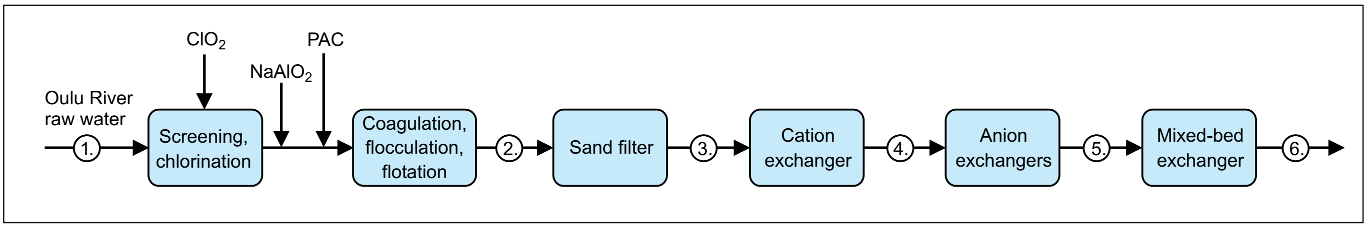

Figure 3:
Plant A water treatment process.
PAC   polyaluminium chloride

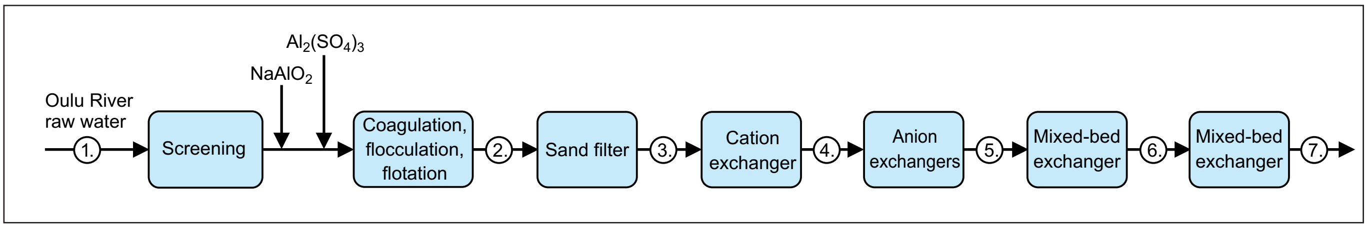

Figure 4:
Plant B water treatment process.

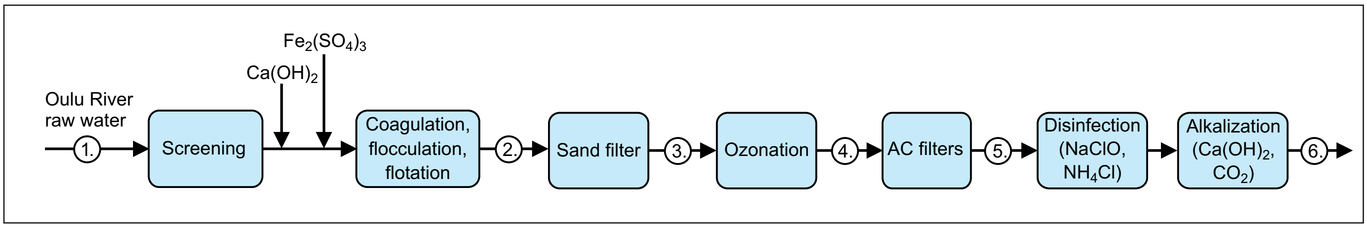

Figure 5:
Plant C water treatment process.

Chemical Analysis

The total organic carbon (TOC, $mg \cdot L^{-1}$) of the water samples was measured with a Sievers 900 Portable TOC analyser according to the manufacturer specifications. TOC samples were collected in acid washed (1 h soaking in 10 % HNO_3 and rinsed with ultrapure water) vials and preserved at 4 °C before being measured. Control solutions with known TOC concentrations were prepared from glucose and measured occasionally to control the proper operation of the analyser. The analyser was also flushed carefully with ultrapure water before measurements to avoid contamination from the instrument itself.

The conductivity of the influent and AC filtered water was monitored online (Kemetron online conductivity probe) and the values were logged directly to a computer. Conductivity data was then manually edited to remove peaks which were the result of regeneration of ion exchange units or stopping of the water flow. Silica concentrations were also monitored online (Bran & Lübbe 6-channel analyser) during full scale AC tests.

The compositions of selected water samples were determined with the liquid chromatography – organic carbon detection (LC-OCD) method, which possesses a detection limit of 1 $\mu g \cdot L^{-1}$ as TOC. Details of the LC-OCD method are explained in [15]. Samples were again collected in acid washed bottles and preserved at 4 °C before being analysed.

RESULTS AND DISCUSSION

Comparison of Water Treatment Processes Using the Same Raw Water Source

Plant C (Figure 5) supplies potable water while plants A and B (Figure 3 and 4) produce demineralized process water. The main differences in the processes are the coagulation-flocculation chemicals employed and the use of an ozone-AC combination at plant C. A comparison of the results of the three water treatment processes is shown in Figure 6. The comparison is based on three series of samples collected over the period 24.09.2009 – 20.10.2009.

As expected, raw water at all three plants had practically the same TOC level (11.7–11.9 $mg \cdot L^{-1}$) during the sampling period. There is a remarkable seasonal TOC variation in the Oulu River as shown in Figure 7. Plant C has a more efficient coagulation-flocculation-flotation stage (78 % TOC reduction) than plants A and B (71 % reduction). One possible reason for this is the ferric sulphate coagulation chemical used at plant C since ferric-based coagulants generally remove NOM better than aluminium-based chemicals [16–18]. AC filtration at plant C only reduced the TOC level by 17.4 %, which was due to long operation cycles. The AC filter had already been in use for 4.5 years at the time of sampling. The ion exchange series at plants A and B removed a substantial part of the remaining TOC. As expected anion exchangers removed most of the TOC since electrically charged NOM is usually anionic because of carboxyl groups. Finally the MB exchangers acted as polishing filters and removed 69 % of the remaining TOC present at plant B and 5.2 % present at plant A. It is possible that anion exchangers were not working efficiently at plant B during the sampling.

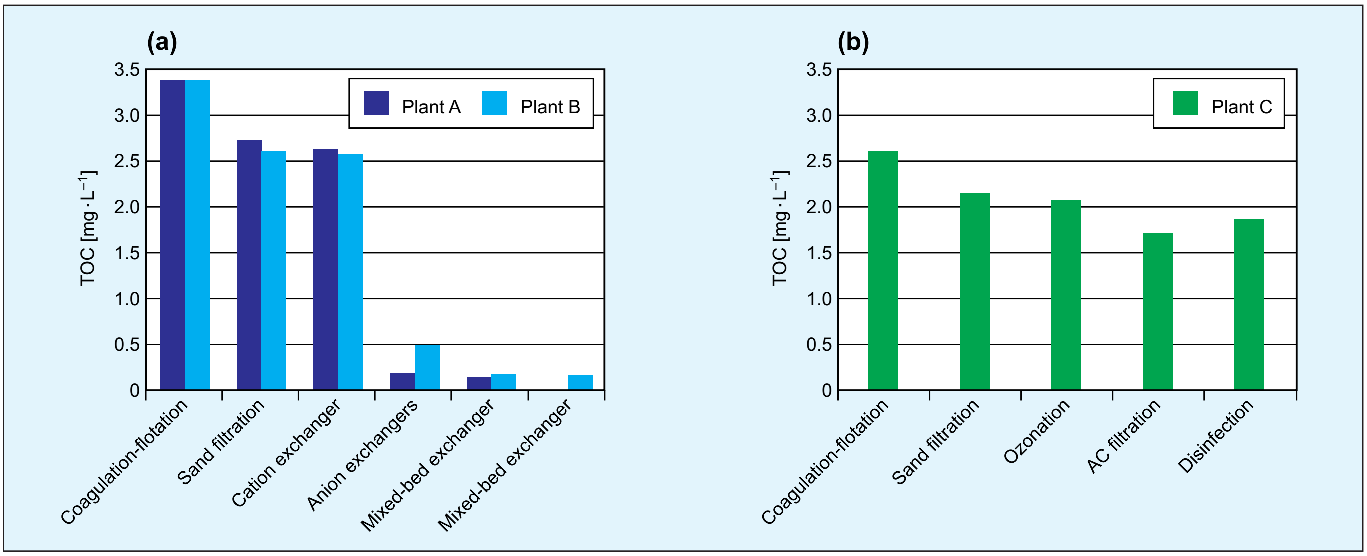

Figure 6:
Comparison of TOC levels after each process stage for all three water treatment plants using the Oulu River as a raw water source. Samples were collected between 24.9.2009 – 20.10.2009.

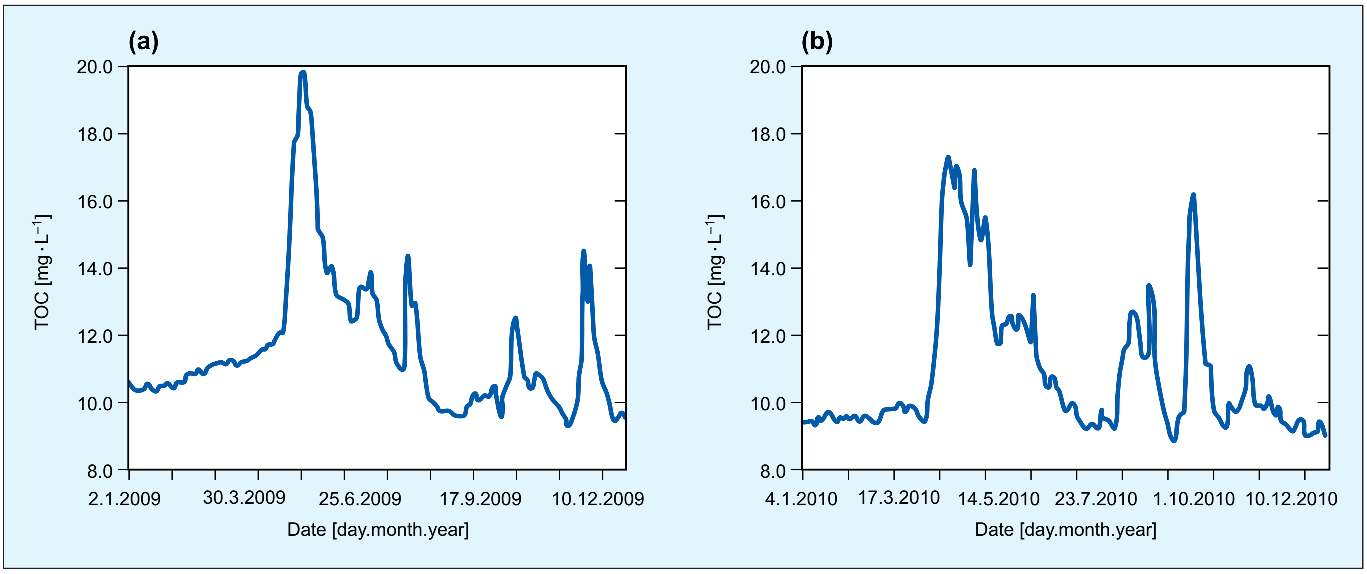

Figure 7:
Oulu River TOC levels in 2009 (a) and 2010 (b).
Data was provided by Oulu Waterworks.

Activated Carbon Filtration

The results of TOC measurements during the pilot scale AC filter tests are presented in Figure 8a. Overall, the first AC filter removed 38–70 % of TOC, the MB unit up to 12 % and the second AC filter up to 13 %. Furthermore, the MB unit and especially the second AC filter occasionally increased the TOC level (Figure 8a). The role of the second AC filter after the MB unit seems to be insignificant in terms of TOC reduction, however dissolved organic carbon (DOC) levels measured with the LC-OCD method showed that the second AC filter removed a substantial part of residual DOC (Table 1). The role of the MB unit is important since conductivity increases extensively in an AC filter (Figure 9a). The MB unit removes ionized inorganic material which is released from the AC bed. However, the identity of this ionized material remains unclear.

TOC reductions measured in the full scale AC filter are shown in Figure 8b. The TOC reductions were between 40–65 % and were slightly higher than those measured with the pilot scale filters. The conductivity of filtered water (Figure 9b) increased similarly as with the pilot scale

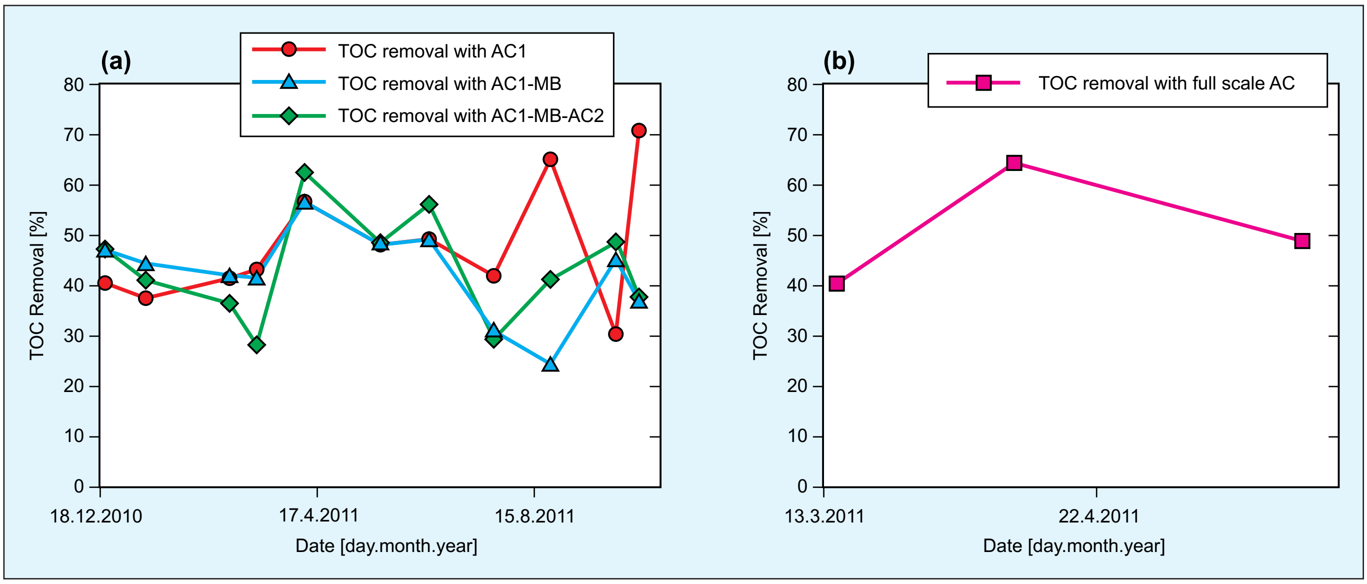

Figure 8:
TOC measurement results of pilot (a) and full scale AC filter tests (b).

	DOC	Hydrophobic	Hydrophilic				
			Biopolymers	Humic substances	Building blocks	LMW neutrals	LMW acids
Raw water	7 832	635	155	4 758	1 267	976	41
Chemically treated water	3 136	541	56	803	1 038	698	n.d.
Demineralized water	155	29	22	n.d.	26	72	5
AC1 filtered water	62	2	18	n.d.	9	31	3
After pilot MB	125	n.d.	32	n.d.	30	49	14
AC2 filtered water	37	n.d.	14	n.d.	5	17	2

Table 1:
Composition of organic compounds in different parts of the plant A water treatment process. Samples were collected on 22.9.2011. All concentrations are stated in $\mu g \cdot L^{-1}$.
n.d. = not detectable (< 1 $\mu g \cdot L^{-1}$); LMW = low molecular weight

filters and so a subsequent MB unit was needed to reduce conductivity. The conductivity sensors used were not as accurate as the ones used with the pilot scale experiments so the actual conductivity values (Figure 9b) are not comparable with the readings in Figure 9a. The silica level of filtered water (Figure 10) was initially 212 $mg \cdot L^{-1}$ with a new AC bed, however it took about 14 days for the silica levels to settle to a constant value of 20 $mg \cdot L^{-1}$. By positioning the MB unit after the AC filter, the remaining silica was reduced to a concentration of 0.002–0.005 $mg \cdot L^{-1}$.

It was hypothesized that if an AC filter could operate biologically, then the conductivity increase would be due to the conversion of organic carbon to carbonate. However, colony forming unit (CFU) counts of the AC filtered water showed that there was no or insignificant biological activity. The CFU increase in the AC filter was

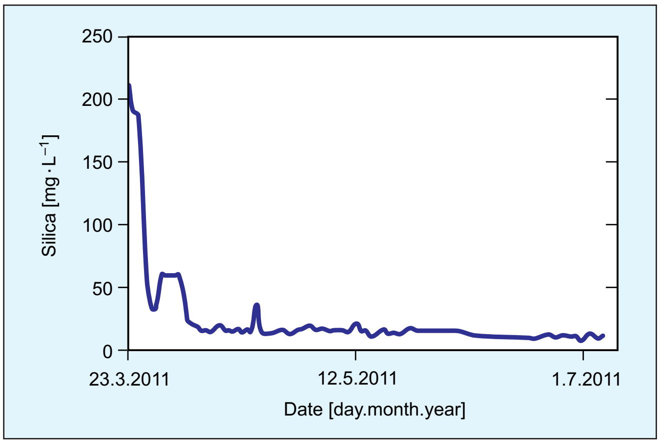

Figure 10:
Online silica measurement results of water after full scale activated carbon filter.

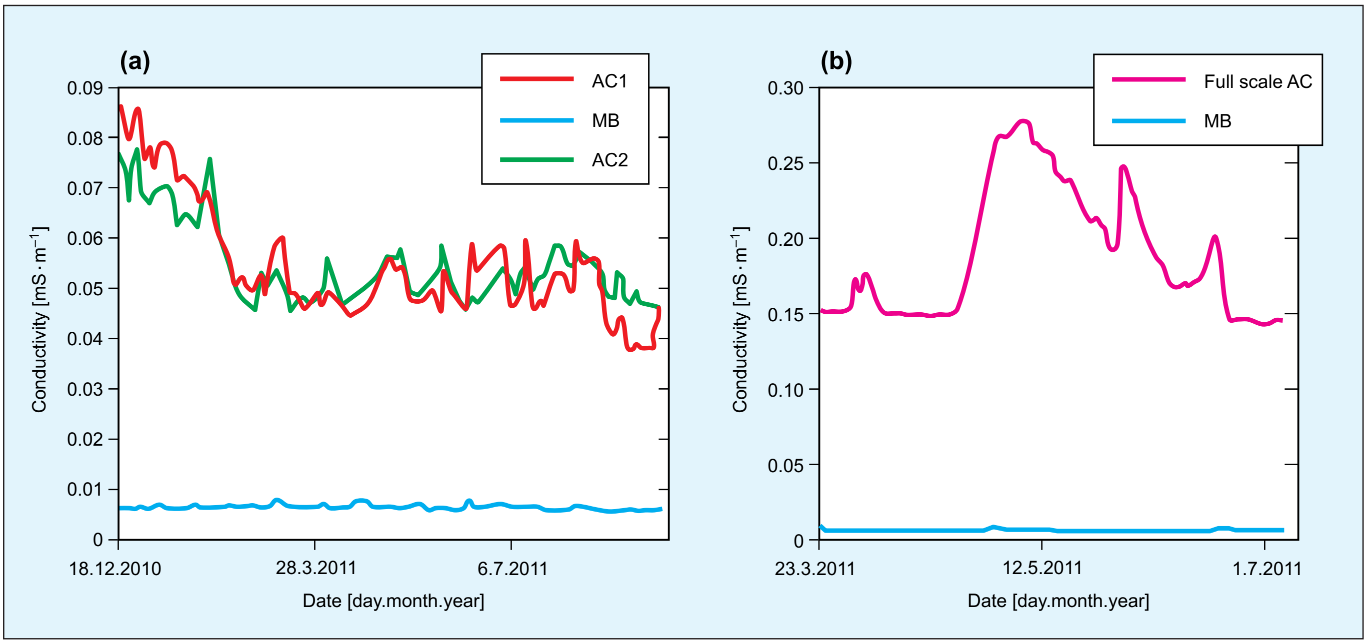

Figure 9:

Conductivity of water:
a) after pilot scale activated carbon filters (AC1 and AC2) and mixed-bed ion exchanger (MB), and
b) after full scale activated carbon filter (AC) and mixed-bed ion exchanger (MB).

	DOC	Hydrophobic	Hydrophilic				
			Biopolymers	Humic substances	Building blocks	LMW neutrals	LMW acids
Raw water	8 410	n.d.	169	5 833	1 259	1 140	9
Chemically treated water	2 646	100	74	835	1 009	619	8
Demineralized water	145	n.d.	21	n.d.	20	102	2
AC1 filtered water	109	n.d.	23	n.d.	15	70	n.d.
After pilot MB	86	n.d.	22	n.d.	12	51	1

Table 2:

Composition of organic compounds in different parts of the plant A water treatment process. Samples were collected on 9.12.2010. All concentrations are stated in $\mu g \cdot L^{-1}$.

n.d. = not detectable ($< 1\ \mu g \cdot L^{-1}$); LMW = low molecular weight

only 25 CFU per ml maximum. Furthermore the nutrient content of demineralized water is too low to allow microorganisms to accumulate. This is actually beneficial as microbial activity in the AC bed could possibly endanger the water quality.

Composition of Organic Compounds

The compositions of organic compounds at different stages of the plant A water treatment process are shown in Tables 1 and 2. Organic compounds are divided into hydrophobic and hydrophilic fractions, in which the latter is divided into biopolymers ($>> 20\,000\ g \cdot mol^{-1}$), humic substances ($1\,000\ g \cdot mol^{-1}$), building blocks, e.g. decomposition products of humic substances, ($300–500\ g \cdot mol^{-1}$), low molecular weight (LMW) neutrals ($< 350\ g \cdot mol^{-1}$) and LMW acids ($< 350\ g \cdot mol^{-1}$).

Raw water has high levels of humic substances as do most Finnish surface waters. The problematic fractions are biopolymers, building blocks and LMW neutrals, which comprise 1/6 of the DOC. These fractions are characterized by an electrically neutral structure, which is the reason why ion exchange cannot remove them effectively. The AC and MB units remove these fractions in part, resulting in a DOC level of 86 $\mu g \cdot L^{-1}$ (Table 2) in the produced water. After about 10 months of continuous use other sets of samples were analysed and it was discovered that the AC1 filter performance had actually improved. However, the pilot MB unit has started to release organic material, probably because it has reached its ion exchange capacity. Interestingly though, AC2 removes a substantial part of the residual DOC, which can't be seen with the TOC measurements (Figure 8a). The final DOC concentration with an AC-MB-AC set-up is comparable to the DOC achieved with reverse osmosis.

CONCLUSIONS

Based on the results of pilot and full scale AC filtration experiments, the following conclusions can be made:

- Activated carbon filtration with acid washed AC is a suitable method for the reduction of residual TOC in demineralized water both in pilot and full scale.
- TOC removal of 38–57 % was achieved in activated carbon filter produced water; the TOC level ranged between 150–200 $\mu g \cdot L^{-1}$. DOC determined with the LC-OCD method was between 62–109 $\mu g \cdot L^{-1}$.
- With the AC-MB-AC set-up, as low as 37 $\mu g \cdot L^{-1}$ of DOC was achieved after 10 months of continuous operation.
- Organic fractions removed with AC were mainly decomposition products of humic substances (so-called building blocks) and low molecular weight neutral organic compounds.
- The AC bed releases silica and substantially increases the conductivity of the water.
- The AC filter needs a subsequent mixed-bed ion exchanger, which acts as a polishing filter. The role of the mixed-bed unit is to reduce conductivity and remove silica.
- There was no sign of reduction in the TOC removal efficiency in the pilot scale AC filters during the test period of 11 months.

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