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# Efficiency of the activated carbon filtration in the natural organic matter removal

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**Abstract**

The removal and transformation of natural organic matter were monitored in the different stages of the drinking water treatment train. Several methods to measure the quantity and quality of organic matter were used. The full-scale treatment sequence consisted of coagulation, flocculation, clarification by flotation, disinfection with chlorine dioxide, activated carbon filtration and post-chlorination. High-performance size-exclusion chromatography separation was used to determine the changes in the humic substances content during the purification process; in addition, a UV absorbance at wavelength 254 nm and total organic carbon amount were measured. A special aim was to study the performance and the capacity of the activated carbon filtration in the natural organic matter removal. Four of the activated carbon filters were monitored over the period of 1 year. Depending on the regeneration of the activated carbon filters, filtration was effective to a degree but did not significantly remove the smallest molar mass organic matter fraction. Activated carbon filtration was most effective in the removal of intermediate molar mass compounds (range 1000–4000 g/mol). Regeneration of the carbon improved the removal capacity considerably, but efficiency was returned to a normal level after few months.


*Keywords:* High-performance size-exclusion chromatography (HPSEC); Natural organic matter (NOM); Water purification; Activated carbon (AC) filtration

## 1. Introduction

Diverse organic compounds generated by the biological processes both in a water body and in a surrounding watershed are found in all surface waters. These compounds are referred to as the natural organic matter (NOM). One common approach for characterizing NOM is to divide the mixture into the hydrophilic and hydrophobic fractions. The hydrophilic fraction includes, e.g. carboxylic acids, carbohydrates and proteins, while the hydrophobic fraction includes so-called humic substances (HS) (Croue et al., 2000). HS is a term referring to a broad class of interrelated compounds, including, for example, humic and fulvic acids. Compositions of HS vary from source to source with respect to, e.g. solubility and reactivity (Aiken et al., 1985; McCreary and Snoeyink, 1980).

NOM is important in a water treatment process due to its role as precursor to the formation of chlorination by-products as well as its role in the concentration and transport of inorganic and organic pollutants (Collins et al., 1986). NOM can be removed from water by traditional treatment processes such as chemical coagulation, or by advanced techniques like activated carbon adsorption and nanofiltration (NF) (Owen et al., 1995). The high molar mass (HMM) matter is proved to be more amenable to removal in the coagulation/flocculation process than the low molar mass (LMM) material, particularly that fraction with an apparent molar mass (AMM) of <500 g/mol (Matilainen et al., 2002; Collins et al., 1986). Coagulation prior to the granular activated carbon (GAC) filtration removes particles that might clog the GAC filter. Coagulation also removes NOM, which reduces the loading on the GAC filters (Jacangelo et al., 1995). Previous studies

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have shown that coagulation can significantly increase both bed life and the adsorptive capacity of NOM on GAC (Semmens et al., 1986; Hooper et al., 1996).

GAC is an effective adsorbent used widely for drinking water treatment. Its main use is the removal of micro-pollutants such as pesticides, industrial chemicals, tastes and odors and algal toxins (Newcombe, 1999). The adsorption of compounds to the GAC is influenced by the structural and the chemical characteristics of the carbon surface (Newcombe, 1999; Karanfil et al., 1999). GAC adsorbs NOM to some degree (Jacangelo et al., 1995). The adsorption behaviour of NOM is particularly difficult to understand due to its heterogeneous nature (Newcombe, 1999). McCreary and Snoeyink (1980) noticed that the extent of adsorption of the HS decreased with increasing total carboxyl groups. In many studies the LMM matter was noticed to be more amenable for adsorption than the HMM organic matter mainly due to size exclusion effect (McCreary and Snoeyink, 1980; Karanfil et al., 1999; Newcombe et al., 2002). According to study by Newcombe et al. (2002) the adsorption of NOM is controlled predominantly by the relationship between the molecular size distribution (MSD) of NOM and the pore size distribution of the carbon. The lifetime of the GAC filters can be expanded by reactivation of the carbons (Hyde et al., 1987). However, the thermal reactivation can result in an enlargement of the macropores in the carbon because of burn-off effects and increase the removal of the HMM organics and decrease the LMM matter removal (Boere, 1992).

Chlorine dioxide ($ClO_2$) is used in the water treatment train mainly as preoxidant and disinfectant. The application of GAC adsorption subsequent to water preoxidation by $ClO_2$ may lead to the formation of organic by-products due to interactions between GAC, NOM and $ClO_2$ (Swietlik et al., 2002). Swietlik et al. (2004) noticed that $ClO_2$ caused a break-up of the large molecules and altered the MSD of NOM towards smaller molecules. On the contrary, oxidation with small doses of $ClO_2$ can increase the molar masses (MM) of some organic matter molecules (Swietlik et al., 2002). Swietlik et al. (2002) also demonstrated that even a small dose of $ClO_2$ may significantly influence the adsorptivity of the NOM onto GAC. They concluded that after $ClO_2$ oxidation the HMM NOM adsorbed on the GAC filter to the higher level in comparison with the unoxidized NOM. The adsorption of the LMM (<500 g/mol) NOM was decreased after $ClO_2$ oxidation. Their explanation was that part of the LMM NOM was insignificantly affected by the oxidant. Therefore this fraction was relatively polar and did not absorb onto the carbon surface.

The aim of this study was to measure the organic matter content and its transformation in the water treatment train. The high-performance size-exclusion chromatography (HPSEC) fractionation was used as the measuring technique. In addition to HPSEC, also some conventional methods were used. Special attention was paid to the monitoring of the efficiency of the GAC filtration to remove NOM, and the influence of the age and regeneration of the filters on the NOM removal capacity.

## 2. Materials and methods

### 2.1. Rusko Water Treatment Plant

The raw water for the treatment plant is pumped from the Lake Roine, 7 km southeast of the plant. Lake Roine is approximately 52 $m^2$ wide and 25–35 m in depth. The raw water intake pipe goes to the depth of 4–5 m, 200 m from the shore. The Rusko Water Treatment Plant produces 65% of the distributed drinking water for the city of Tampere, Finland. The maximum treatment capacity is 55 000 $m^3$/day and an average water flow is about 1400 $m^3$/h. The raw water source is fairly typical surface water source in Finland: alkalinity is low (about 0.25 mmol/l), turbidity is fairly low (about 2 FTU) and the NOM content measured as total organic carbon (TOC) is approximately 5 mg/l. The treated water has a TOC value of about 2.5 mg/l.

The treatment process at Rusko consists of chemical addition ($Al_2(SO_4)_3$), which was added 25–33 g/$m^3$, followed by flocculation and clarification with flotation, chlorine dioxide ($ClO_2$) disinfection, GAC filtration, and post-chlorination (Fig. 1). The purpose of the $ClO_2$ addition is to disinfect the water and to control taste and odor problems and it was added 0.2 g/$m^3$. Chlorine gas is used in post-chlorination to yield a free chlorine residual of 0.3 mg/l in the purified water.

### 2.2. GAC filters

The 14 GAC filters are ordinary one-layer filters and each of them has a surface area of 30 $m^2$ and a bed depth of about 115 cm. All similar in structure, the filters are so-called sand replacement filters, in which the GAC replaces the sand to mechanically filter and remove odor and taste from water. The filter contact time with water is 15 min (1600 $m^3$/h). The filters are flushed with water and air after about 40 h of use and the GAC is regenerated every couple of years. Carbons are changed after about three regenerations because the aluminum accumulates into the filter and cannot be removed in regeneration.

In this research four of the filters (characterized in Table 1) were studied. The types of the filters B and C were Filtrasorb TL 820 and filter D Filtrasorb 200. Carbons in filters B and D were changed before the start of the study. Filter C was regenerated twice before the study and during the study in May 2001. Filter A was Aqva Sorb BG-09 and regenerated twice before the study.

### 2.3. Sampling procedure

Water samples were taken once a week between the middle of September 2000 and the end of September 2001, a total of 12 months. Samples were taken from the following stages of the treatment sequence: (1) raw water, (2) water after the flotation, prior to $ClO_2$ addition, (3) water after four parallel AC filters (AC-A, AC-B, AC-C and AC-D) before chlorination, and (4) combined purified water from all 14 GAC filters (see Fig. 1). Basic water analyses were done at the day of the sampling. The 10 ml samples were collected and frozen until analysed with HPSEC and $UV_{254}$ during the year 2001.