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Application of organic matter fractionation technique for evaluation of coagulation-biofiltration process at a full scale WTP

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***Abstract*— Biofilters at water treatments plants (WTP) are responsible for biologically stable water, but their effectiveness can be influenced by various factors. To determine the efficacy of the biofiltration process, so-called, natural organic matter (NOM) fractionation technique can be used, which enables the evaluation of distribution between hydrophobic and hydrophilic organic groups. Additionally, several methods were used for determination of living microorganisms in biomass of biofilters. The results of the current study showed that the biodegradation and biological activity processes in biofilters at WTP do not occur. The live microorganisms represented only 28% of the total cell count, which was 50% than reported. Nevertheless, NOM fractionation methods used in this research can be easily applied and useful for evaluation of full scale biofilter activity.**

***Keywords*—biofilters, biomass, biostability, fractionation**

I. Introduction

Due to relatively cold climate and abundance of soils and pits rich in organic carbon, the concentration of natural organic matter (NOM) in Latvia is higher than in many European countries [1]. During water disinfection NOM forms toxic and carcinogenic by-products and easily biodegradable organic carbon compounds (low molecular weight organic substances) which serve as a substrate for water microorganisms [1,2,3].

To control the removal of NOM during water treatment not only the total concentration of organic substances but also their composition should be known. For example, organic substances with a high concentration of aromatic groups – mostly humic substances, are usually removed during coagulation [4], whereas biologically degradable organic carbon (BDOC) is better removed during biological filtration [5]. Nevertheless, simple classification into humic substances and BDOC is not always informative for water treatment plans with high NOM in raw water.

In order to optimize coagulation and biofiltration processes at WTP it is necessary to evaluate not only the total organic carbon concentration, but also the specific fraction distribution after each water treatment process. To determine the efficacy of the biofiltration process so-called natural organic matter fractionation methods can be used in combination with several other methods for determination of living microorganisms in the biomass of biofilters. The fractionation of NOM allows to evaluate the distribution of the high and low molecular weight (or hydrophobic and hydrophilic) organic groups.

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The aim of this study was to characterize biofilter efficacy with rapid NOM fractionation technique in a full-scale water treatment plant located in Latvia and using humic rich raw water source for production.

II. Materials and Methods

A. Water sample collection

The WTP (supplying approximately 100000 m^3/d and located in Riga, Latvia) takes the raw water from the River Daugava. The water has low turbidity and and high content of organic matter. The water is treated with pre-ozonation (1-3 mg/l), chemical coagulation (average dose of 7-10 mg Al/l, pH 6.7-7.2), rapid sand filtration, main ozonation (2-8 mg/l) and biologically active carbon (BAC) filtration. The empty bed contact time (EBCT) of biofilter is 20-30 min. Finally a chlorine gas (0.5 – 1.0 mg/l of free chlorine) is added for disinfection. The samples were collected every week for the period of one month during the cold season (from 21.11.2013 to 16.12.2013) from all the treatments steps of Daugava WTP in Riga, Latvia.

B. TOC and dissolved organic carbon (DOC) determination

TOC and DOC measurements were performed using a TOC-5000A Analyser and autosampler ASI-5000 (Shimadzu Corporation, Kyoto, Japan) based on high temperature and acidification of the sample and by the difference of the total carbon and inorganic carbon measurement, according to the standard method [6]. For DOC determination samples were filtered through 0.45 μm pore size membrane filters (Millipore Corporation, USA). Each sample was tested in duplicate and the mean values were calculated (CV≤2%). The blank and control solutions were analyzed with each series of sample in order to verify the accuracy of the results obtained by the method. The minimal detection limit (MDL) was 380 μg/l.

C. NOM structure analysis

The NOM structure analysis was performed according to the procedure described by Chow et al. [7]. The sample (500 ml) filtered through a 0.45 μm membrane was acidified to pH 2 with concentrated HCl and passed through the column with adsorbent resin DAX-8. A sample from column effluent (60 ml) was collected for the DOC analysis and the remaining effluent was passed through the column with adsorbent resin XAD-4. The very hydrophobic acids (VHA) and slightly hydrophobic acids (SHA) were determined as

the difference between the initial and effluent DOC from DAX-8 and XAD-4 columns, respectively. The effluent from XAD-4 was adjusted to pH 8 with 10 M NaOH and passed through a column packed with adsorbent resin IRA-958. The charged hydrophilic acids (CHA) were determined as the difference between the initial and effluent DOC from IRA-958 column. Finally, neutral (NEU) fraction was determined as the DOC concentration of IRA-958 effluent.

D. *Total bacterial counts*

Biofilter material samples were obtained from two randomly selected biofilters. Biofilter media samples were treated with ultrasonic processor (2 minutes at 20 µA and 22 KHz, Cole Parmer) and then fixed with 3-4% formaldehyde for at least 20 minutes. Then the sample (0.1 – 0.5 ml) was filtered onto 25-mm-diameter 0.2-µm-pore-size filters (Anodisc; Whatman plc) and washed with 50 ml of sterile distilled water. Without removing the membrane from the filtration unit, the sample was stained with 10 µg/ml DAPI (4', 6-diamidino-2-phenylindole, Merck, Germany) for 15 – 20 minutes in the dark. Then the stain was removed by washing with 50 ml of sterile distilled water. After washing the sample was removed from filtration unit and air-dried. Cell numbers were determined by epifluorescence microscopy by counting 20 random fields of view (Ex: 340/380 nm; Em. > 425 nm, dichromatic mirror 565 nm, Leica DM6000B). The results were expressed as amount of cells per g of sample.

E. *Heterotrophic plate counts*

Decimal dilutions of samples (treated with ultrasound as for determination of total bacteria count) were performed in sterile distilled water and then inoculated onto R2A agar (Oxoid Ltd, UK) plates by spread plate technique. All plates were incubated in dark at 22°C for 7 days. The results were expressed as colony forming units (CFU) per ml of sample.

F. *Flow cytometry analysis*

Biomass samples were stained with 10 µl/ml SYBR Green I (Invitrogen, USA) dye (1:100 diluted with DMSO, (Sigma-Aldrich, USA)) and were kept in the dark for 15 minutes. To determine the cell counts CyFlow instrument (Partec, Hamburg, Germany) equipped with 200 mW laser, emitting a fixed wavelength of 488 nm, and volumetric hardware was used. Green fluorescence (FL1) was collected at 640 nm, red fluorescence (FL3) at 650 nm and all data were analyzed with the Flomax software (Partec). All samples were processed at speed 500 µl/min. Unless stated otherwise, the instrument settings and electronic gates were kept the same for all samples in order to achieve comparable data.

III. Results and discussions

The average concentration of total organic carbon (TOC) in the river water was 12,97±2,97 mg-C/l. Dissolved organic carbon represented 88-99% (11,86±1,88 mg-C/l) of TOC. NOM at the source consisted mainly of the VHA and SHA factions (data not showed), which are mostly hydrophobic humic substances. During the treatment the average TOC concentration decreased from 12.97 to 6.57 mg/l and DOC from 11.86 to 6.62 mg/l.

Water treatment significantly reduced the VHA faction (59%). During the ozonation-coagulation and rapid sand filtration VHA fraction decreased from 5.19 to 0.89 mg/l and increased again to 0.98 mg/l after biofilters. Combination of ozonation process with biological treatment has the advantage on reduction of biological regrowth, because biological treatment can remove biologically active organic matter selectively [8]. Ozone is breaking high molecular weight organic matter into low molecular weight organic matter, this way increasing the biodegradability of NOM [8], but this process is slow. Due to the decrease of the size of the molecules, ozonation may also have negative effect on the NOM adsorption on BAC [9]. Significant increase of CHA fraction concentration (from 24% to 35%) after ozonation and NEU fractions (from 14 to 31%) after the rapid sand filters were observed.

For the characterisation of NOM removal during biofiltration, the samples were collected before and after biofilters of Daugava WTP. The Results showed that the reduction in DOC concentration in the biofilters is low (4% the biodegradable fraction of the DOC). The average DOC concentration in the biofilter inflow water samples was 6.99 mg/l and in outflow - 6.62 mg/l. CHA concentration decreased from 2.88 mg/l to 2.66 mg/l, and at the same time NEU substance concentration decreased from 2.04 mg/l to 1.93 mg/l. Thus, NOM fractionation results showed that VHA/NEU fractions did not change during BAC filtration process. Only transformation of SHA/CHA fraction occurred. This means that mineralization (transformation to CO_2) of organic matter did not occur in the biofilters. The low efficacy of the biofilters may be linked to the high residual concentration of ozone (0.31 mg/l) and low temperature during the sample period. The water temperature in biofilter outflow samples was 14.0 °C in week 1, 11.0 °C in week 2, 5.2 °C in week 3, 3.5°C in week 4, 3.6 °C in week 5. The results of the fractionation in the biofilter outflow samples can be seen in Fig 1. When the temperature of water was the lowest (week 4 and 5) the CHA fraction increased during the biofiltration process. Possibly the flushing of previously adsorbed CHA took place.

> The rapid fractionation techniques appeared to be useful approach to monitor water treatment efficacy of NOM in humic rich waters

The amount of microorganisms in biomass of the biofilters was determined using several methods. Results showed that total cell count determined by DAPI method was 8.27×10^9 cells/1 g of filter material; living micro-organisms as determined by flow cytometry analysis was 2.33×10^9 cells/1 g of filter material and the colony forming units - 1.17×10^9 cells/1 g of filter material, representing 28%

and 14% of the total count accordingly. The biofilm on the filter material was distributed evenly and the average microbial count was 2.27×10^9 cells/1 g of filter material in the upper layer of the filter, and 2.15×10^9 cells/1 g of filter material at 1 m depth. The amount of viable microorganisms in the upper layer of the filter is less than 27%, at a depth of 1 m - 38%. At the same time cultivable microorganism counts in the top filter layer is higher (16% of the total count) than at 1 m depth - 10%. The observed differences can be explained by the negative effect of the ozonation (viable counts) and starvation in the lower layers of the biofilters (cultivable counts).

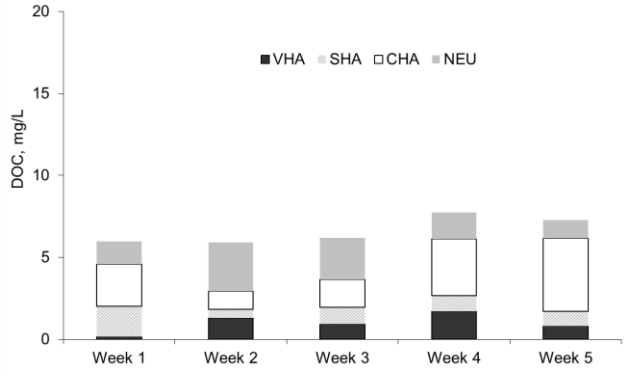

Figure 1. Changes of DOC fraction in outflow from biofilter during the experimental period.

During the study it was found that the average cell count in biomass isolated from biofilters was 5.66×10^9 cell per 1 g of filter material. Viable microorganism fraction consisted of only 28% of the total cell count. This is 50% lower than previously reported results [10].

So, low efficiency of the biofilters may be linked to the high residual concentrations of ozone before biofilters (average concentration of 0.31 mg/l) and low water temperature (3.5 ° C), which was identified during this study.

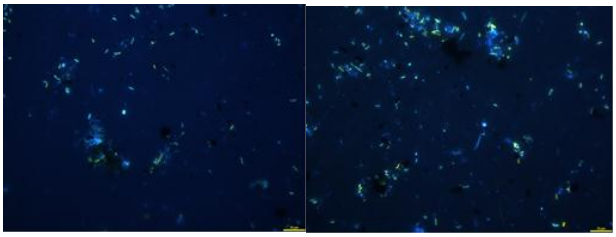

Figure 2. Biofilm of the biofilters captured with a fluorescent microscope (Ex: 340/380 nm; Em. > 425 nm, dichromatic mirror 565 nm, Leica DM6000B): biofilter 1 (left, 0.1 ml) and biofilter 2 (right, 0, 1 ml).

Analyses of the biofilm samples using DAPI method (Figure 2) showed that biofilter biomass cells form clusters with small particles of the filter material. All samples contained a lot of fluorescent inorganic particles, which interfered with the counting process. Samples from the 1 m depth represent much greater cell species diversity - small, shaped and very long cells, but their total number is lower than in the upper layer samples.

IV. Conclusions

The rapid fractionation techniques appeared to be useful approach to monitor water treatment efficacy of NOM in humic rich waters.

The average DOC concentration in the biofilter inflow water samples was 6.99±0.90 mg/l and outflow - 6.62±0.79 mg/l. CHA concentration decreased from 2.88 mg/l to 2.66 mg/l, and at the same time NEU substance concentration decreases from 2.04 mg/l to 1.93 mg/l

The average plate count biological filter material is $5.66\text{x}10^9$ cells per 1 g of the filter material. The amount of viable microorganisms was only 28% from the total cell count.

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