Improving Organic Micropollutant Removal of Activated Carbon by Pre-treatment with Zeolite Adsorbent

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ABSTRACT

Activated carbon (AC) is commonly used in drinking water treatment plants (DWTPs) to remove organic micro-pollutants (OMPs), and it is effective in adsorbing a wide range of OMPs. However, its adsorption efficiency can be affected by natural organic matter (NOM). NOM is a complex matrix and widely exists in water bodies. During the drinking water treatment process, the large size fraction of NOM may block the pore of the granular activated carbon (GAC), and the small size fraction of NOM can compete with OMPs and occupy the sites.

The goal of this study is to increase the OMP adsorption efficiency of AC filtration in the drinking water treatment process. The objective was to investigate the feasibility of the competitive NOM removal by zeolite adsorption prior to powdered activated carbon (PAC). Meanwhile, the filtration performance and advantages of nanofiltration (NF) with 1000 Da membranes were found out. Zeolite - AC and NF- Zeolite - AC combined treatments were exterminated.

In this study, the properties of zeolites were reviewed and the zeolite with FAU framework was selected as the hydrophobic adsorbent. Batch experiments with FAU and PAC were conducted to examine the adsorption performance of 10 common OMPs in different water samples. Comparative batch tests on UV effluent and NF permeate were carried out with two stages, zeolite pre-treatment and PAC treatment. Ultrapure water and demineralized water were involved as the reference to prove the influence of NOM from adsorption isotherms. Dissolved organic carbon (DOC) measurements were provided by the DWTP.

NOM is confirmed to hinder the OMP adsorption on AC according to DOC measurements and adsorption isotherms. NOM smaller than 1000 Da is proved to cause the competition with OMPs. FAU-type zeolite pretreatment was failed to remove the competitive NOM removal.

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1 Introduction

Organic pollutants (OMPs) are a range of natural and anthropogenic chemical species and are widely introduced into environmental compartments like soil and water (Loos et al., 2010). OMPs are increasing in water sources and considered as an emerging problem in drinking water production. OMPs may cause various water borne diseases, and OMP removal in drinking water treatment plants (DWTPs) is gaining extensive attention (Ahmad, Naeem, Ahmad, Usman, & Al-Wabel, 2019).

Natural organic matter (NOM) is a complex group of organic compounds, which are mainly derived from plant decay process (Bhatnagar & Sillanpää, 2017). It exists ubiquitously in water bodies and rises the problems in the drinking water, for instance, deteriorating the taste, odor and color, causing fouling in membranes, etc. The removal of NOM is becoming a challenging issue worldwide. In this case, the OMP adsorption on AC is observed to be diminished by the existence of NOM in the feed water. This is mainly attributed to two mechanisms, pore blockage and site competition in AC.

Granular activated carbon (GAC) is widely applied to remove OMPs as the last treatment process in most of DWTPs. Powdered activated carbon (PAC) is applied in this experiment to accelerate the process due to the duration limitation. Only competition effect of the NOM can be measured in micropores of PAC. High-silica zeolites are hydrophobic and selective adsorbents, FAU framework zeolite is chosen in this study.

Evides Waterbedrijf ^{TM} supplies drinking water to over 2.5 million consumers in the Netherlands. Nowadays, it aims at investigating treatment combinations to improve OMP removal efficiency through AC filtration, facing the problem of NOM. Membrane filtration or adsorbent dosing are considered as efficient preceding processes before AC filtration. GAC is utilized as the last unit of the conventional treatment process in the full-scale plant of *Evides* ^{TM} (Fig 1.1). Meanwhile, *Evides* ^{TM} *is* now running a pilot plant using capillary nanofiltration (NF) with 1000 Dalton membranes prior to AC in Kralingen (Fig 1.1).

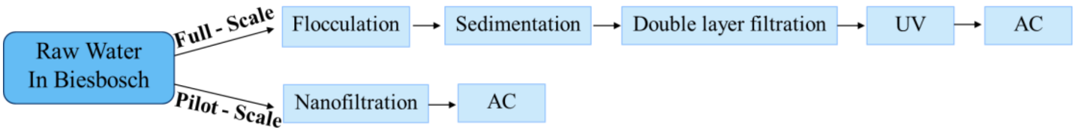


Fig 1.1 Scheme of *Evides*^{TM} drinking water purification process in Kralingen, full-scale plant and pilot-scale plant

The objective of this study is to improve the AC efficiency by zeolite pretreatment, and to investigate the advantages of NF. It is hypothesized that with the pretreatment of FAU adsorption, the NOM effect on the competition can be effectively mitigated, leading to the higher efficiency of PAC. The effect of NOM on OMP adsorption on AC are aimed to be exterminated by batch experiments. Zeolite - AC and NF- Zeolite - AC combined treatment experiments are therefore designed and conducted.

2 Background and theory

2.1 Adsorbent characterizations

2.1.1 Activated carbon

Granular activated carbon (GAC) is the most popular and widely utilized adsorbent in drinking water and wastewater treatment plant. It is composed of good porous structure and large surface area from 600 to 2000 m^2/g, resulting in it can adsorb the solutes with a wide range of diameter and type (Bansal & Goyal, 2005; Marsh & Reinoso, 2006). In practice, drinking water treatment plants (eg. *Evides Waterbedrijf* ^{TM}) consider the GAC adsorption as the typical process after the disinfection to remove the organic micro-pollutants (OMPs), disinfection by-products (DBPs) and other residual contaminant in water and improve the color and taste (Bhatnagar, Hogland, Marques, & Sillanpää, 2013).

2.1.2 Zeolites

Zeolites are crystalline aluminosilicates with SiO_4 and AlO_4 framework in a tetrahedral structure, where Si^{4+} or Al^{3+} is in the center and connected with oxygen atoms(Auerbach, Carrado, & Dutta, 2003; Jacobs, Flanigen, Jansen, & van Bekkum, 2001). Zeolites are widely used in water treatment as selective adsorbents, owing to they are porous materials in which micropores (pore diameter are less than 2nm) are at the uniform size and regular distribution (Li & Yu, 2014). The properties of zeolites are determined by their synthesis and framework. According to Jiang (N. Jiang, Shang, Heijman, & Rietveld, 2018), high-silica zeolites with FAU, MFI, MOR and BEA framework, the commonly used OMP adsorbents are reviewed in this study.

Synthesis

Zeolites synthesis is characterized by the silica to alumina mole ratio (Si/Al ratio), which is equal to half of the SiO_2/Al_2O_3 ratio. The properties of zeolites with the same framework type vary owing to the different Si/Al ratio, which divides zeolites into high-silica (Si/Al ratio up to several thousands) or low-silica groups (Si/Al ratio < 2), describing the hydrophobicity of zeolite surface (Nan Jiang, Shang, Heijman, & Rietveld, 2019; McCusker & Baerlocher, 2001).

Surface hydrophobicity is defined as the repelling capacity to polar molecules, especially water (Olson, Haag, & Borghard, 2000). In this case, it will inhibit the blockage of the water clusters in the pore of zeolites and improve the sorption capacity(de Ridder, Verberk, Heijman, Amy, & van Dijk, 2012). According to various authors, the more Al content in the compounds, the higher affinity to the water (Bolis, Busco, & Ugliengo, 2006; Olson et al., 2000). Therefore, a high Si/Al ratio always indicates the higher hydrophobicity. It can be concluded that high-silica zeolites are always selected as the higher efficiency adsorbents of solute removal (Anderson, 2000; Grieco & Ramarao, 2013; Lienert, Güdel, & Escher, 2007).

Currently, high-silica zeolite is proved to adsorb on OMP in water effectively (Damjanović, Rakić, Rac, Stošić, & Auroux, 2010). However, its application in the full-scale water treatment plant still has not been realized (N. Jiang et al., 2018). On the other hand, the low-silica groups have strong polar contributing to the capacity to interact with water and are applies as desiccants or softener (Newsam, 1986).

Framework

The framework of zeolites describes the connectivity of the atoms in the tetrahedral structure affected by pore opening, cage and channel (McCusker & Baerlocher, 2001).

- Pore opening of the zeolites is the entry of a cage or channel, determining the pore size, the diffusion and accessibility of adsorbates (Koubaissy et al., 2012). Zeolites consist of atoms connecting each other as a ring, the larger the number of atoms, the bigger the pore size. Accordingly, zeolites can be described as n-ring with n T or O atoms, for instance, FAU has a 12-ring framework with size 7.4 * 7.4 Å (0.74 nm) (see table1).

- The cages are the polyhedral units in zeolites and channels are the aggregation of these linked polyhedral units. They determine features of zeolites such as surface area and pore volume, etc. The accessible area is defined as the area that the center of the water molecule is available to access in an ideal situation (Foster, Rivin, Treacy, & Delgado Friedrichs, 2006). As shown in table 1, FAU is composed of 3-dimensional cages, with an internal diameter of 13 Å and encircled with 4 openings (Baerlocher, McCusker, & Olson, 2007).

Table 1 shows the framework-related characteristics of FAU, MFI, MOR and BEA, with the order from higher pore volume (FAU) to lower (MFI). The selected zeolites have a highly accessible area from 834 to 1220 m^2/g. The one with lower density always has larger pore volume, which is highly correlated to the adsorption capacity. Considering those four commonly used zeolites, the framework of FAU consists of the largest pore opening size and 3-dimensional cages, leading to the largest accessible area and maximum sphere diameter can be included.

2.2 Organic pollutant characterizations

This study investigates two kinds of ubiquitous pollutants in the water: OMPs and NOM.

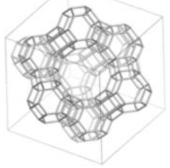
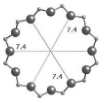
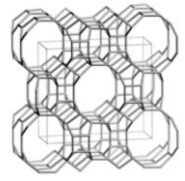
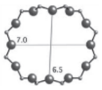
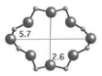
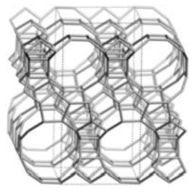
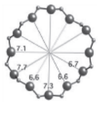
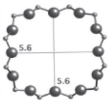
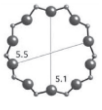
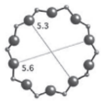
OMPs are originated from pesticides, pharmaceuticals and personal care products. It is becoming widespread in water bodies owing to the unregulated and continuous release. The accumulation of OMPs and by-products in the aquatic environment can increase potential environmental and health risks, such as interfacing endogenous hormone systems and bacterial resistance (Gavrilescu, Demnerová, Aamand, Agathos, & Fava, 2015). Ten OMPs are involved in this study: Acesulfame, Atrazine, Caffeine, Hydrochlorothiazide, Gabapentin, Lidocaine, Sulfadimethoxine, Sulfamethazine, Sulfamethoxazole, and

Theophylline. The general properties of these OMPs are listed in *Appendix B*.

Aquatic NOM widely exists in all kinds of water bodies and becomes one of the main pollutants in the water treatment process. NOM predominately consists of carbon at a fraction of 40-60%, which constitutes more than half of to the DOC in water (Świetlik, Dąbrowska, Raczyk-Stanisławiak, & Nawrocki, 2004). The main NOM component is attributed to humic substances, which are only rejected by low molecular weight cut off (MWCO) membranes. The hydrophobic NOM can be removed by adsorption.

NOM is found to be detrimental since it is able to worsen the taste and color of water, become the precursor of the disinfection by-products (DBPs) and consume the dissolved oxygen (DO) in water (Bhatnagar & Sillanpää, 2017). In present studies, how to efficiently and completely remove the NOM in the drinking water process is still a challenge which needs to be solved.

Table 2.1 Properties of FAU, MFI, MOR and BEA

Framework type & Chemical formula	Framework structure [a]	Pore opening [a]	Ring number and pore opening size [a] (Å × Å)	Maximum diameter of a sphere can be included (Å) [b]	Framework density (T atoms (/Å^3)) [a]	Accessible area(m^2/g) [b]
FAU			12 rings 7.4×7.4	11.24	12.7	1211.42
MOR		 	12 rings 6.5×7.4 8 rings 2.6×5.7	6.70	17.2	1010.22
BEA		 	12 rings 6.6×6.7 12 rings 5.6×5.6	6.68	15.1	1220.45
MFI		 	10 rings 5.1×5.5 10 rings 5.3×5.6	6.36	17.9	834.41

[a] (Baerlocher et al., 2007)

[b] (Foster et al., 2006)

3 Materials and methods

3.1 Materials

The entire experiment was supervised and conducted in the Water Lab of TU Delft. Different materials applied in this experiment, adsorbents, water samples and organic micropollutants are introduced in this section.

Adsorbents

As mentioned in section 2.1.2, FAU framework has the largest pore opening size and accessible area with high hydrophobicity. Accordingly, it was selected as the best pretreatment adsorbent. The powder FAU zeolite (code 390HUA, 250 Al/Si ratio, 630 m^2/g surface area, 0.05 wt % Na_2O content) used in this study is originated from Tosoh Corporation (Tokyo, Japan) (Fig 3.1).

Evides Waterbedrijf ™ water company provided the granule activated carbon (GAC) from its full-scale plant in Kralingen, the Netherlands. To increase the adsorption rate and reduce the experiment period, the GAC was grinded into powder manually by a mortar (Fig 3.2).

Fig 3.1 PAC from Evides™

Fig3.2 FAU (390 HUA)

Water samples

Various types of water samples are aimed to be tested to obtain different adsorption series and transverse comparison. Ultrapure water and demineralized water were supplied by the Water Lab. *Evides*™ company provided two kinds of water from its treatment plant in Kralingen, one water type is the influent of GAC from its full-scale plant, which is the effluent of UV treatment, after flocculation, sedimentation and the double layer filtration. Another water source is the effluent of the capillary nanofiltration pilot plant, which is directly fed by the original water from Biesbosch's reservoirs. NF permeate and UV effluent was sampled and delivered to the Water Lab at 17th, July 2019 and stored in the fridge at 4°C.

Organic micropollutants

For the organic micropollutants (OMPs), technical grade (>98% purity) Acesulfame, Atrazine, Caffeine, Hydrochlorothiazide, Gabapentin, Lidocaine, Sulfadimethoxine, Sulfamethazine, Sulfamethoxazole, and Theophylline were purchased to the Water Lab, their structure and chemical properties are reported in the previous section, table x.

3.2 Preparation

Prior to batch experiments, adsorbents of PAC and FAU were previously dried in an oven at 105 °C over 12h, to avoid the effect of the surface water contained. Adsorbents were cooled in the desiccator for 1h then.

A 5 μg/L of OMP mixed solution was prepared to amplify the experiment effect. A stock suspension was applied as an effective method to accurately distribute the low amount of PAC, which can also reduce the volume of the required solutions and flasks. The preparation of those solutions is elaborated in *Appendix C*.

3.3 Equilibrium batch adsorption experiments

In this study, equilibrium adsorption was determined in batch experiments, adsorption kinetics were not performed. The critical process of this experiment is to treat different types of water samples with and without zeolite pretreatment under the same PAC conditions. By comparing the corresponding adsorption efficiency of OMPs through adsorption isotherms, whether zeolite adsorption on NOM is valid can be inferred.

For ultrapure water and demineralized water, NOM removal by zeolites prior to PAC does not make sense because these kinds of water barely contain any NOM. Therefore, only PAC was applied to deal with the ultrapure water and demineralized water.

For NF permeate and UV effluent, two series of comparison experiments were conducted, respectively (Fig 3.3). One was firstly adsorbed on the zeolite and then on the PAC, the other was directly treated with PAC.

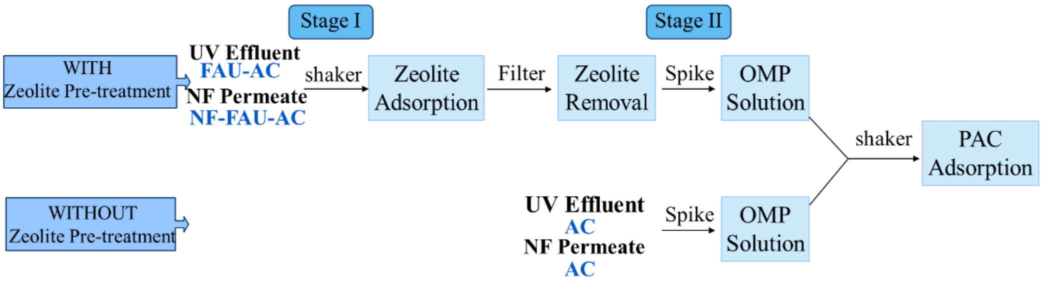


Fig 3.3 Experimental scheme of NF permeate and UV effluent

The adsorption experiments were conducted in batch mode in the constant temperature tower in the Water Lab, keeping 20°C during the entire experiments (Fig 3.4). The equilibrium adsorption tests were carried out in a shaker and the bottles were shaken at a constant rate. Consequently, a contact time of 48 hours was employed to guarantee the equilibrium state would be reached.

Fig 3.4 The shaker used for 48 hours adsorption experiment

For the UV effluent and NF permeate, two series of experiments were implemented, with and without zeolite pretreatment. Only the second stage for PAC adsorption experiment is significant for ultrapure or demineralized water.

At the first stage, a 3 L Schott bottle was filled with 2.5 L corresponding water and dosed 2500 mg FAU, at a concentration of 1000 mg FAU /L. The solution was thermostatically and continuously shaking 48 hours during equilibration. The zeolites were separated from the aqueous solution by vacuum filter through 0.47 μm GF/F filters (Fig 3.5).

At the second stage, 2000 mL of the filtered sample was transferred into a 3 L Schott bottle, followed by spiking 2 mL of the OMP solution at a concentration of 5 μg/L. Meanwhile, 2000 mL of the untreated target water sample in another 3 L Schott bottle was spiked of the same amount of the OMP solution. The OMP solution was filtered through a syringe filter containing 0.45 μm PFTE membranes in advance, to get rid of the undissolved particles and ensure the solution stability. In this stage, the solutions either treated with or without zeolite would be added PAC and start shaking at the same time. Batch experiments in this stage were conducted in a series of 250 mL Schott bottles with a sequence of PAC dosage from 0 to 300 mg/L. For each batch, 100 mL of total solution was contained, with a certain amount of water sample solution and stock suspension. The stock suspensions of PAC were kept stirring on the magnetic plates, and 200-2000 μL of them were accurately dosed into the batches, see table B in *Appendix C* for the specific PAC dose range, solution and stock volumes (Fig 3.6). Then 48 hours adsorption test was conducted.

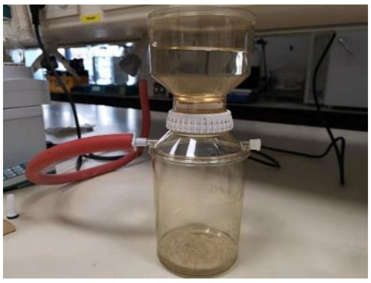


Fig 3.5 The filter used for zeolite removal in the first stage

Fig 3.6 Two stock suspension solutions of AC

After 48 h adsorption experiments, around 1 mL of the water samples were filtrated through a syringe filter to remove particles and collected into glass vials for LC-MS measurement. In this study, a reference measurement (0 mg PAC/L) was included by the average of 3 blank samples in each isotherm series.

3.4 Measurement

The level of NOM can be deduced through TOC and DOC measurements, providing the basis of the entire analysis. LC-MS was utilized for every sample to obtain the OMP concentration for the adsorption isotherm. Meanwhile, the pH of the samples was measured through a HACH pH meter to prove the normal situation of the water samples during the experiment.

3.4.1 DOC and TOC measurement

TOC and DOC are the overall and dissolved organic matter content in water, respectively. They are considered as the general measured data in water quality related studies, which can indicate the level of NOM. DOC information of the previous year was provided by *Evides*^{TM} from its DWTP. TOC-V_{CPH} from *SHIMADZU*^{TM} in the Yellow Lab of TU Delft was applied for TOC measurement (Fig 3.7). The raw water samples (UV effluent and NF permeate) and those after PAC treatment were detected on 3rd September 2019. The concentration of PAC was 100mg/L, which was selected as the suitable maximum dosage. The measurement was based on the combustion catalytic oxidation/NDIR method, according to the manual of the device.

Fig 3.7 TOC - V_{CPH} in the Blue Lab of TU Delft

Fig 3.8 LC-MS device in the Blue Lab of TU Delft

3.4.2 LC-MS analysis

Prior to the analysis, internal standard solutions and calibration standard solutions were prepared, which track the analyte and determine the calibration line, respectively. See *Appendix D* for the specific preparation work.

Liquid chromatography-mass spectrometry (LC-MS) combines the physical separation capacities with mass analysis capacities, and it was applied to measure the residual OMP concentration after adsorption. LC-MS is in the Blue Lab of TU Delft and originated from *Waters*^{TM} (Fig 3.8). Before measuring, the internal standard solution was added into each water samples and calibration standard solutions at 1 µg/L, see details in *Appendix C*. When setting the sequence of measurement in the Masslynx, the calibration line was firstly determined, and the calibration line standards were detected again at last to improve the accuracy. The operation and setting of LC-MS were referred to the manual *"Instruction manual for LC-MS MassLynx and TargetLynx"*.

3.5 Adsorption model

The adsorption isotherm displays the amount of adsorbate adsorbed on the surface of the adsorbent. To determine the adsorption isotherm, the following equations were applied. In this study, the amount of OMP adsorbed per unit mass (q_e, µg/mg) can be calculated as:

$$q_e = \frac{(C_0 - C_e)m}{V}$$

where

C_0, C_e: the initial and equilibrium concentration of adsorbates, µg/L

m: the mass of the adsorbent, mg

V: the volume of the adsorbent, L

The nonlinear Freundlich isotherm is widely used as an empirical model assuming the concentration of adsorbate adsorbed the surface of adsorbent rises according to the increase of adsorbate concentration. It can be applied for multi-layer adsorption concerning energetic surface heterogeneity. The nonlinear Freundlich equation is written as (Freundlich, 1906):

$$q_e = K_F C_e^n$$

where

K_F: temperature-dependent constants, represents the adsorption capacity, (mg/g)/(mg/L)^n

n: temperature-dependent constants, represents the adsorption intensity

The nonlinear Freundlich equation can be logarithmically linearized and K_F, n are obtained from linear regression:

$$\log q_e = \log K_F + n \log C_e$$

4 Result and discussion

4.1 DOC and TOC analysis

Evides^{TM} provided DOC measurements in its DWTP during the previous years. Table 4.1 lists the data at the sampling time (2019/7/17) and the average data of the whole period. There is no significant difference between the daily data and the annual data, except the fact that DOC in the PAC filtrate will increase for a longer operation time of the carbon filters.

The raw water stored in Biesbosch is pretreated naturally and its quality highly depends on the weather conditions. As introduced in section 1, NF is directly fed with Biesbosch's raw water, UV is together with a series of preceding conventional treatment processes. Notably, NF (1000 Da) removed large organic matters with high efficiency of 78% from the feed water in Biesbosch. In contrast, UV effluent still contained more large size fractions of DOC, around 25% of compounds were removed. GAC can adsorb partial residual DOC. Based on the data, GAC had an adsorption efficiency of 44% and 30% of the DOC in NF permeate and UV effluent, respectively (Table 4.2). The various efficiency of GAC is caused by the existence of NOM, illustrating that NF can promote GAC efficiency to some extent. Nevertheless, this improvement is not significant comparing 44% to 30%. It may indicate that the larger size fractions of NOM removed by NF does not dominate the influence on GAC efficiency. NF is effectively to remove parts of NOM (>1000 Da) which may cause the blockage, however, the small size fractions which contribute to the competition with OMPs still obviously diminish the GAC removal efficiency.

Table 4.1 DOC measurements (mg/L) provided by *Evides^{TM}*

Date	Raw water from Biesbosch	NF permeate	GAC filtrate (fed with NF permeate)	UV effluent	GAC filtrate (fed with UV effluent)
Sampling time 2019/7/17	3.89	0.84	0.47	2.91	2.04
Average (2018/9/19-2019/8/21)	3.77	0.82	0.35	2.72	1.66

Table 4.2 Removal efficiency of different treatment processes based on DOC data (2019/7/17) provided by *Evides^{TM}*

NF	GAC filter (fed with NF permeate)	UV and preceding treatment processes	GAC filter (fed with UV effluent)
78.41%	44.04%	25.19%	29.90%

TOC was measured in the WaterLab either in the raw water sample or the AC filtrate sample to compare with the company's data. The measurements almost show the same DOC level as it in the *Evides^{TM}* plant (Table 4.3), which confirm the accuracy of this research.

Table 4.3 TOC measurements (mg/L) of different water samples at 2019/09/03

Water types	Raw water from *Evides*^{TM}	PAC (100mg/L) filtrate
NF permeate	0.81	0.43
UV effluent	2.56	2.01

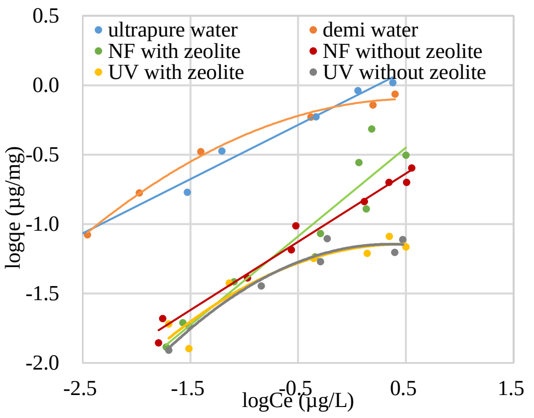
4.2 Adsorption isotherms

The adsorption isotherms were plotted to define the adsorption capacity of the zeolite pretreatment on different OMPs. Linear Freundlich model fits the results by calculating $logq_e$ and $logC_e$, while the parameters K_f and n are not obtained owing to the non-ideal fitted curves. Parts of the 10 OMPs (Acesulfame, Caffeine, Atrazine and Gabapentin) show a reasonable curve which is discussed in this section, others are displayed in *Appendix E*.

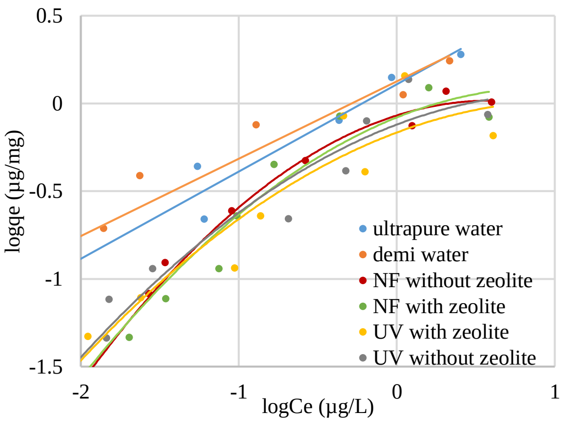
For Acesulfame and Caffeine, the entire measurements are contained in the graphs as Figure 4.1 (a-b). Only the higher values of the Atrazine and Gabapentin are plotted in Figure 4.1 (c-d), and lower-value points are scattered which might be inaccurate since they were below the limit of LC-MS measurement.

The adsorption behavior of those 4 OMPs all shows that isotherms of the ultrapure water and demineralized water are on the above. It confirms that the existence of NOM hinders the OMP adsorption by PAC, compared to the reference water with trace concentration of NOM.

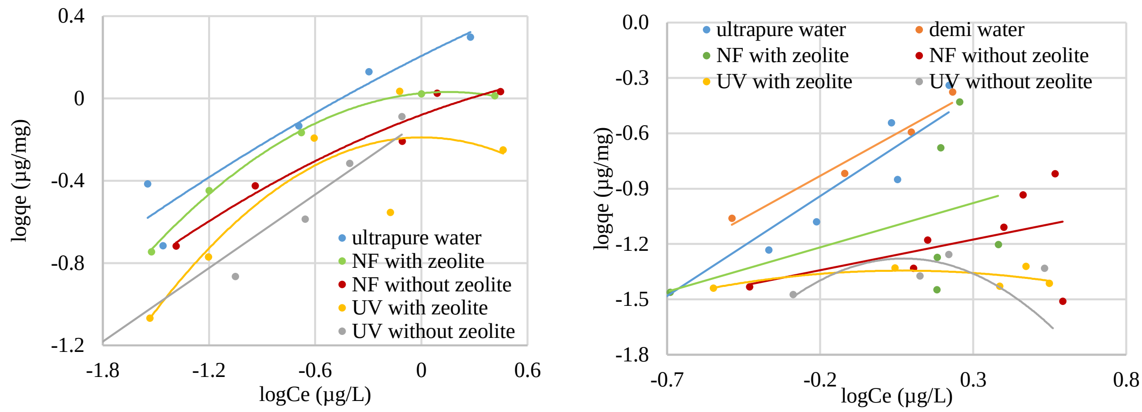
Meanwhile, 4 graphs display that the OMP adsorption in NF permeate is slightly better than in UV effluent in different degree. It confirms the DWTP's results of DOC values as discussed in the previous section. NF is more effective in removing organic matters and can promote AC efficiency. However, both for NF permeate and UV effluent, there were no obvious advantages of zeolite pretreatment, even if the NF had already removed the NOM larger than 1000 Da. It can be deduced that the small size fraction of NOM contributes to the lower efficiency of OMP adsorption in PAC. Thus, the NOM smaller than 1000 Da might be the part causes the site competition with OMPs in PAC. Probably, the small size fraction may be not able to be retained in the FAU with the largest included size at 11.2 Å.



(a) Acesulfame



(b) Caffeine



(c) Atrazine (d) Gabapentin

Fig 4.1 Adsorption isotherms

4.3 Suggestions of the adsorption experiment

- All experiments should be conducted in duplication or triplication to reduce the error.

- GAC provided by *Evides*^{TM} was grinded manually into PAC by a mortar, which was not entirely homogeneous. During the addition of AC stock suspension, the larger AC particles might block the tip of the pipette, which influenced the experiment and lead to some systemic error. In a further study, GAC should be grinded through the machine.

- The speed of the shaker used in the constant temperature tower was slow due to the device limitation, compared to a stirrer. Especially for the 3L Scotter bottle, where zeolite pre-treatment experiments were performed, it is better to use a stirrer to ensure complete adsorption.

5 Conclusions

The efficacy of NOM removal by FAU-type zeolite was evaluated based on the treatment process of NF or UV, from *Evides* ^{TM} DWTP. The adsorption performance was obtained and discussed based on the DOC, TOC analysis and adsorption isotherms. The conclusions are summarized as the following:

- According to DOC measurements provided by the DWTP where applies GAC, NF can effectively remove around 80% DOC of the raw water and the conventional treatment processes removed 25%. Comparing the adsorption efficiency of GAC fed with NF permeate and UV effluent, it increased only 14% and reached 44% through NF. The results indicate that NF has a high removal efficiency of organic matters (>1000 Da) which may cause the blockage of GAC. However, the small size fraction of NOM competing with OMPs still obviously reduces the GAC removal efficiency. The competition is caused by NOM smaller than 1000 Da.

- There was an obvious difference between the adsorption isotherms of ultrapure water or demineralized water and UV effluent, where the reference water isotherms were always on the above. It proves that NOM diminishes OMP adsorption on PAC.

- Competition of NOM with OMPs was measured through this study by applying PAC. According to isotherms, the OMP adsorption efficiency of PAC was slightly increased through NF treatment. Thus, NF might reject a small part of NOM causing the competition with OMPs. But it did not show significant improvement with zeolite pretreatment. It demonstrates that FAU has no effect on removing competitive NOM. Probably, the small size fraction of NOM seems like not be retained by zeolites. It also confirms that NOM smaller than 1000 Da mainly causing the competition.

- For the target combined treatment processes, both zeolite - AC and NF - zeolite - AC lack the efficacy of NOM removal, which is contrary to the hypothesis.

In conclusion, NOM can compete with OMP and decrease the OMP adsorption efficiency of AC. The competition is done by molecules smaller than 1000 Da in the small micropores of AC. FAU-type zeolite pretreatment has no advantages on the competitive NOM removal. And it is not feasible to improve the AC efficiency by applying FAU-type zeolite pretreatment.

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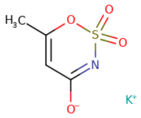
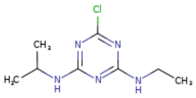
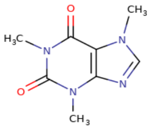
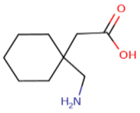
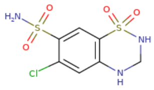
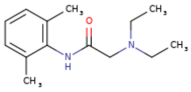
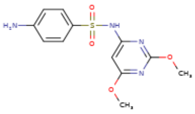
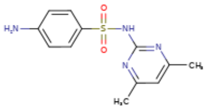
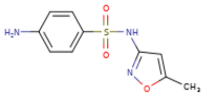
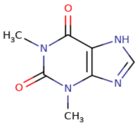
Appendix A List of abbreviations

AC	Activated carbon
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
DWTPs	Drinking water treatment plants
FAU	Faujasite
GAC	Granular activated carbon
LC-MS	Liquid Chromatography–Mass Spectrometry
MWCO	Molecular weight cut off
NF	Nanofiltration
NOM	Natural organic matter
OMPs	Organic micropollutants
PAC	Powdered activated carbon
TOC	Total organic carbon
UV	Ultraviolet

Appendix B General properties of ten target OMPs

Table B General properties of ten target OMPs

Structure	Chemical name	Molecular formula	CAS	Molecular weight (g/mol)	Water solubility (g/L)
	Acesulfame K	$C_4H_5NO_4S$	55589-62-3	201	270 (20°C)
	Atrazine	$C_8H_{14}ClN_5$	1912-24-9	216	0.035 (26°C)
	Caffeine	$C_8H_{10}N_4O_2$	58-08-2	194	21.6 (25°C)
	Gabapentin	$C_9H_{17}NO_2$	60142-96-3	171	4.49 (25°C)
	Hydrochlorothiazide	$C_7H_8C_lN_3O_4S_2$	58-93-5	298	0.72 (25°C)
	Lidocaine	$C_{14}H_{22}N_2O$	137-58-6	234	4.1 (30°C)
	Sulfadimethoxine	$C_{12}H_{14}N_4O_4S$	122-11-2	310	0.34
	Sulfamethazine	$C_{12}H_{14}N_4O_2S$	57-68-1	278	1.5 (29°C)
	Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	723-46-6	253	0.61 (37°C)
	Theophylline	$C_7H_8N_4O_2$	58-55-9	180	7.36 (25°C)

Source: ChemIDPlus

Appendix C Preparation of solutions

Micropollutant solution

The initial concentration of each of OMPs was around 5 μg/L, obtained through the following procedures. Due to the normal concentration of OMPs in the water is too low to detect, 5-6 mg of the set of micropollutants were dosed as a mixture into 1L ultrapure water, at 5 mg/L micropollutant solution. Afterwards, it was spiked into the target volume of the water sample to achieve 5 μg/L of OMPs. By this way, all batches were able to start with the same micropollutant concentration. Ultrasonication was used for slightly heating to ensure all compounds were dissolved well. Moreover, the solution was kept over 1 day to mix well, and aluminium foil was used due to some OMPs are sensitive to the light.

Stock suspensions

With the ultrapure or demineralized water experiments, the low doses of the adsorbent are essential because the adsorption is higher due to the lack of competition. In this study, 1 mg/L was considered as the lowest dose. But in case of a 250 ml flask, 0.25 mg of the activated carbon is needed to weigh, which is a low amount. A stock suspension is applied as an effective method to accurately distribute the low amount of adsorbents, which also reduces the volume of the required solutions and flasks.

In this study, the PAC concentration was varied between 1 and 300 mg/L. 2 stock suspensions were conducted using a magnetic stirrer, with 1000 (stock1) and 20000 (stock2) mg PAC/L, respectively.

Table C PAC dosage, stock volume and corresponding water sample with OMP solution volume

Batch No.	**Ads dose [mg/L]**	**Batch Vol. [mL]**	**V ads stock 1 [μL]**	**V water sample with OMP solution [mL]**	**V ads stock 2 [μL]**	**V water sample with OMP solution [mL]**
0	0	100	-	100	-	
1	1	100	100	99.99	-	
2	2.5	100	250	99.75	-	
3	5	100	500	99.5	-	
4	10	100	1000	99	-	
5	20	100	2000	98	-	
6	40	100	-		200	99.8
7	60	100	-		300	99.7
8	100	100	-		500	99.5
9	200	100	-		1000	99
10	300	100			1500	98.5

Appendix D Preparation of LC-MS analysis

Internal standard mix solution

An internal standard is used to track the analyte in the LC-MS quantitation, based on the certain ratio of peak area of the analyte to that of the internal standard. It also compensates for the losses involved in the matrix or measurement. The internal standard should behave the same as the analyte, and the machine must be able to separate those two compounds (Wieling, 2002). In present work, the same compound as the target one but labelled with isotopes are common uses as a suitable and stable internal standard, for instance, a deuterated compound.

In this study, 6 kinds of isotopically labelled internal standard solutions were firstly prepared in ELGA (ultrapure water) or ACN(CH_3CH) if the substance does not completely dissolve in the low volume of ELGA, at concentrations of 10 mg/L. Then 50 µL each internal standard solutions (iStd.Mix) were mixed with 4700 µL ELGA at a concentration of 100 µg/L, and stored at 4 °C.

Calibration line standard solutions

The calibration line standard is considered as an external standard in this condition. Determining the calibration curve is essential for LC-MS measurement to establish a standard and reference. The standard solutions with a mixture of 10 target OMPs at each concentration from 0 to 10 µg/L were prepared through progressive dilution. See the specific concentration in the following table. By measuring standard solutions at a certain concentration, a linear calibration line was obtained in LC-MS, and applied for the sample measurement.

The instruction of the specific procedure to make the solutions are listed in the following tables.

General prepared solutions			
	Name	Concentration [µg/L]	Volume [µL]
Step 0 a	"single substance stock 0"	*10000*	*1000*
Step 0 b	"single iStd. stock"	*10000*	*1000*
Step 1	"iStd. Mix"	*100*	*5000*
Step 2	"stock 1"	*50*	*1000*
Step 3	"stock 2"	*0.5*	*500*
Step 4	"Samples with iStd. Mix"	*1 (iStd. Mix)*	*500*
Step 5	"Calibration standards with iStd. Mix"		*1000*

iStd. Mix	**Samples**	**Stock 1**	**Stock 2**
total V [µL]	total V [µL]	total V [µL]	total V [µL]
5000	*500*	1000	500
target conc. [µg/L]	iStd. Target conc. [µg/L]	target conc. [µg/L]	target conc [µg/L]
100	1	50	0.5
single iStd. stock conc. [µg/L]	iStd. Mix concentration	single subst. stock 0 conc. [µg/L]	stock 1 concentration [µg/L]
10000	100	10000	50
stock V to add (per iStd.) [µL]	iStd. Mix V to add [µL]	stock V to add (per subst.) [µL]	stock 1 V to add [µL]
50	5	5	5
Number of iStds	-	Number of substances	-
6	-	*10*	-
V Elga to add [µL]	V sample to add [µL]	V Elga to add [µL]	V Elga to add [µL]
4700	495	950	495

Calibration standard solutions				
stock name =>	**iStd. Mix**	**stock 1**	**stock 2**	**ELGA water**
stock conc. [µg/L] =>	100	50c	0.5	-
cali. stand. target conc.	V to add	V to add	V to add	V to add
[µg/L]	[µL]	[µL]	[µL]	[µL]
0	10		0	990
0.0025	10		5	985
0.005	10		10	980
0.01	10		20	970
0.05	10		100	890
0.1	10		200	790
0.5	10	10		980
1	10	20		970
2.5	10	50		940
5	10	100		890
10	10	200		790
Sequence of addition =>	iStd. Mix: 1st	stock: 3rd	stock: 3rd	ELGA water: 2nd

Appendix E Adsorption isotherms for other OMPs