

Super ground PAC in combination with Ceramic Micro- filtration

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Colophon

Title

SUPER GROUND PAC IN COMBINATION WITH CERAMIC
MEMBRANE

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Summary

Ceramic membranes, with their inherent mechanical, thermal and chemical stability with a long life operation, offer an attractive alternative to polymeric membranes in surface water treatment applications despite being expensive. High cost of ceramic membranes can be compensated with its ability to operate at high Fluxes. To do so, the membranes need pre-treatment (coagulation or adsorption with activated carbon) to prevent frequent use of chemicals for membrane cleaning (CEB and CIP). The main goal of this research was to investigate the removal efficiencies of NOM and atrazine with sub-micron Powdered Activated Carbon (S-PAC) and normal (N-PAC) in combination with (ceramic/polymeric) microfiltration. S-PAC was obtained by grinding thermally N-PAC in a novel mill. The S-PAC and N-PAC had an average effective particle size of $0.3\mu\text{m}$ and $2\mu\text{m}$, respectively.

The S- and N-PAC was pre-coated onto the (ceramic/polymeric) microfiltration prior to filtration. Pre-coat layers of 70mg/l and 20mg/l of S-PAC (48 and 14 layers, respectively) and 70mg/l of N-PAC (14 layers) were introduced onto $0.1\mu\text{m}$ MF PVDF membrane placed in Amicon (un)stirred Cell and $0.1\mu\text{m}$ MF Ceramic membrane prior to filtration. DOC, UV_{254} and atrazine were analysed to compare the removal efficiencies of S-PAC and N-PAC. An LDF model was employed to simulate the results of atrazine removal with S-PAC and N-PAC in pure MQ water.

The results showed that atrazine removal from Milli Q water (0.1mg/l) was maintained to 99% with 70mg/l of S-PAC after 1 hour and drop to 80% after 30 minutes with 70mg/l of N-PAC without NOM competition. No breakthrough achieved after 1 hour filtration through S-PAC but with N-PAC it was achieved after 25min. S-PAC (20mg/l) shows better removal of atrazine achieving 98% removal compared with 65% with 70mg/l of N-PAC without competitive adsorption after one hour.

The adsorption of atrazine is affected by competition with NOM but atrazine has a negligible effect on DOC and UV_{254} removal due to low concentration. Atrazine removal drop from 99% (without competition) to 62% (with competition) with S-PAC; and from 65% (without competition) to 55% (under competition) for N-PAC after 1 hour of filtration at the same dose. The contact time was < 1 second.

Alternatively, S-PAC showed better removal efficiency in terms of DOC & UV_{254} (without competitive adsorption) at the same dose and lower dose than N-PAC. S-PAC exhausted ($C = 90\%C_0$) after 90 minutes of Filtration while N-PAC exhausted after 60 minutes when a flux of $145\text{L}/\text{m}^2.\text{h}$ applied to the filtration of Delft canal water. Also, 50% of DOC and UV_{254} removal was achieved after 20 minutes for S-PAC and 30% for N-PAC respectively. The same removal efficiencies was achieved for UV_{254} with competitive adsorption indicating that DOC removal is not affected by the presence of small amount of atrazine. S-PAC might have large surface area resulting into fast adsorption kinetic than N-PAC.

The formation of PAC cake fouling was very rapid in S-PAC than in N-PAC. Total resistance of membrane increases from 3 to $13 \times 10^{11} \text{ m}^{-1}$ in case of S-PAC and from 4.5 to $7 \times 10^{11} \text{ m}^{-1}$ for N-PAC after 1 hour. LC-OCD test carried out after that, showed high removal of biopolymers ($>80\%$) in the first 45 minutes with S-PAC. This is suggesting that there was a physical removal of biopolymers due to straining since the bed porosity of S-PAC layer is $0.045\mu\text{m}$ ($0.15d$) and hence create some sort of straining which removes large molecular weight components of NOM like biopolymers.

However, good results were obtained with pre-coated flat membrane PVDF and not in ceramic. This is suggesting that either PAC layers were not well dispersed in Ceramic membrane and or some of the PAC might remain in suspension and did not take part in pre-coat layer. Therefore, to ensure well dispersing of S-PAC inside ceramic membrane channels is a great challenge for further studies on this topic.

Stimela software package designed by TU Delft, KIWA and HVS employed LDF model, shows similar trend of atrazine removal with laboratory results with S-PAC with breakthrough occurs after 1 hour. The model might be useful for prediction of breakthrough curve behavior for S-PAC; however more laboratory experiments are required to validate the statement.

Keywords: Adsorption, pre-coat layer of S-PAC and N-PAC, Ceramic membranes, Flux, NOM, DOC, UV, atrazine and Stimela

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1.0 Introduction

1.1 Background

The use of membrane technology in surface water treatment for drinking water production is receiving more and more attentions (Lee *et al.*, 2004), (Dong *et al.*, 2006) and (K. Sundaramoorthy *et al.*, 2004). The quality of water produced by membrane, less space occupied by plant, minimum use of manpower and declining of membrane cost are major reasons to opt membrane technology than conventional treatment method (Xia *et al.*, 2007) and (Amy, 2007)

In general, membrane technology is indispensable in 21st century. Ceramic membrane with the advantage of long life span and high flux capability promise a big step in water production technology. Basically, Ceramic membranes apart from cost implications (double to polymeric) have added advantages of outstanding mechanical strength, high resistance against heat and chemicals. Also they can withstand high velocity in hydraulic backwashing

However, the major problem in membrane technology is membrane fouling (Pontie *et al.*, 2006). Fouling in membrane increases operation and maintenance costs by deteriorating the performance of membrane and eventually shortening the membrane life (Pontie *et al.*, 2006). Four different types of fouling are identified as particulate fouling, bio-fouling, organic fouling and scaling (Kennedy *et al.*, 2007).

Natural Organic matter (NOM) is a major causes of irreversible fouling of membranes. The origins of NOM in surface water are aqueous, terrestrial, vegetative waste (products and by-products), and other algal cellular matter (K. Sundaramoorthy *et al.*, 2004). One of the techniques of reducing the membrane fouling is pre-treatment of feed water by coagulation or by adsorption with powdered activated carbon PAC.

MF and UF membranes alone are not efficient enough in removing colour, NOM especially humic substances, synthetic organic chemicals (SOCs), taste and odour. Therefore, UF and MF should be combined with other conventional techniques like adsorption on powdered activated carbon (PAC). The association of adsorption on PAC and UF provides the following benefits: better physical removal of NOM and SOC through optimal use of PAC, reduced sludge volume and reducing membrane (Mozia and Tomaszewska, 2003).

The study done by (Zhao *et al.*, 2005) on Removal of organics and viruses using hybrid ceramic membrane MF system without draining PAC (20g/l) showed that DOC removal of 80% and UV removal of 90% at a flux of about

100L/m².h. Furthermore, PAC cake layer assisted ceramic MF to remove viruses to less than detection limit after 60 days of operation (Zhao *et al.*, 2005).

On the other side, PAC adsorption on organic matter (NOM) and metal ions are the main factors causing the PAC cake layer fouling on PAC-MF hybrid membranes (Zhao *et al.*, 2005). Accumulation of particulates is also causing pore blocking and voids clogging in a membrane as well as in PAC layer.

The research by (Zhao *et al.*, 2005) mentioned the decrease of particle size of PAC during operation due to particle breakage caused by severe collision and friction in aeration condition facilitates PAC cake formation on membrane. Moreover, metal ions play a great role on PAC cake fouling than organic matter. PAC with large size when combined with adsorbed small particulates from raw water brings the most severe PAC cake fouling. Oxidation of Iron II to Iron III during PAC adsorption affects PAC cake resistance more than other metal ions.

The importance of PAC on removal of NOM is not limited to water supply only, but also in waste water. The use of PAC into cross flow micro-filtration system resulting in formation of biological powdered activated carbon (BPAC) due to seeding micro-organisms found to be effective in increasing the sorption capacity for removal of organic matter than the fresh PAC (Seo *et al.*, 1997).

The adsorption of PAC is mainly the function of particle diameter the smaller the size means better adsorption and hence low dose usage. This is strongly supported by (Matsui *et al.*, 2005) in his study he found that 5mg/l of submicron PAC (0.8 μ m) has a better adsorption performance than 40mg/l of Normal PAC with a constant flow of 1.5m/d (62.5L/m².h). Besides, he also found that combination of submicron PAC and coagulant (Alum) improves the removal of NOM from 20% to 50% removal than dosing of PAC alone.

1.2 Problem Identified

The past researches on TOC removal on surface water by using S-PAC in a combine mixed stirrer chamber showed that a contact time of at least 1 min is required for better removal of NOM (Matsui *et al.*, 2005). In plug flow the situation might be different. Therefore, this study went through and compares the efficiency of S-PAC and N-PAC used in the form of pre-coat as a pre-treatment prior to Ceramic membrane filtration looking at NOM (DOC), UV and micro-pollutants (atrazine) removal.

1.3 Research Goals and Objectives

The removal efficiency of NOM, pesticides and fouling reduction by pre-coat layer of PAC is mainly depends on amount of dosage, quality of raw water, temperature, pH, grain size of PAC and contact time. To understand the

removal of NOM and pesticides through adsorption with pre-coat layer of S-PAC and N-PAC for improving the quality of water is major target of this research.

1.3.1 Goal

- To compare the efficient of Normal PAC (N-PAC) and Super PAC (S-PAC) in terms of DOC, UV and pesticides removal with Ceramic Micro-filtration membrane without compromise the high Flux.

1.3.2 Objectives

- To compare the DOC and UV_{254} removal efficiency with N-PAC and S-PAC pre-coat layers at high Flux of 150 l/m².h.
- To determine the fractions of NOM that is removed by adsorption with S-PAC and N-PAC along filtration time.
- To compare the removal of atrazine with pre-coat layers of N-PAC and S-PAC under high Flux without competitive adsorption.
- To analyse the fate of atrazine removal on competitive adsorption with NOM
- Establish the breakthrough and exhaustion curve
- Modelling the results of atrazine removal from MilliQ water.

2. Materials and Methods

2.1 Feed Water

Delft canal water which is surface water was used for laboratory experiments. The typical quality of the raw water is shown by the table below

Table 1: Typical Quality of Delft Water Canal

Parameter	
Turbidity (NTU)	14
TSS (mg/l)	25
DOC (mg/l)	15
UV ₂₅₄ (cm ⁻¹)	0.5

Source: Hamad (2008)- UNESCO IHE

2.2 Cleaning Agents

For backwashing and chemical enhanced backwashing and Cleaning in Place (CIP) the following cleaning agents were used.

- Demineralised water
- Filtered water
- Sodium hydroxide
- Sodium Hypochlorite
- Citric acid

2.3 Pre-treatment

Super ground Powdered Activated Carbon (S-PAC) with effective size of 0.3 μ m and Normal Powdered Activated Carbon (N-PAC) with effective size of 2-3 μ m was used as pre-treatment prior to ceramic membrane filtration in terms of pre-coat layers.

2.4 Membrane Material and Equipment

Two types of membrane were used, Ceramic Microfiltration membrane and 0.1 μ m PVDF membrane.

2.4.1 Ceramic Membrane

Monolithic ceramic membranes manufactured by NGK Insulator Ltd of Japan with the following specifications was used

Table 2: Specifications of Monolithic Ceramic Membrane

Description	Parameter
Size (Diameter x length of module)	30mm x 1,000mm
Membrane channel (channel diameter and no. of channels)	2.5mm and 55 channels per module
Membrane surface area	0.4m ²
Norminal pore size	0.1 µm
Operating TMP	5 - 100 kPa
Backwashing Pressure	500 kPa
Filtration duration	6 - 12 hrs
Filtration condition	Dead end mode

Other accessories accompanied with membrane module are

- Gear pump, model Verdergear VG 1000 + pump for in dosing
- Flow meter, model Endress + Hauser
- Pressure gauges, model Endress + Hauser
- Commpressed air pressure vessel
- Automatic Data logger connected to a computer with software (Trend Reader Standard vl. 22). Monitoring of flow, pressure, temperature and time is possible by using data logger.
- Dosing tanks
-

2.4.2 MF PVDF membrane

Characteristics of MF PVDF membrane is shown by Table 3 below:-

Table 3: Specifications of MF PVDF Membrane

Thickness µm	125
Porosity %	70
Filter Material	Hydrophylic PVDF
Pore size µm	0.1
Wettability	Hydrophilic
Water Flow Rate, L/m ² .h	1500
Bubble Point at 23 ⁰ C	≥4.8 bar

2.5 Experimental Set-up

2.5.1 Ceramic Membrane set-up

The pilot plant has four processes that can be either operated automatically or manually. These processes are Filtration, Backwashing, Air Flushing and Forward Flushing. The set up of the pilot plant is shown below:

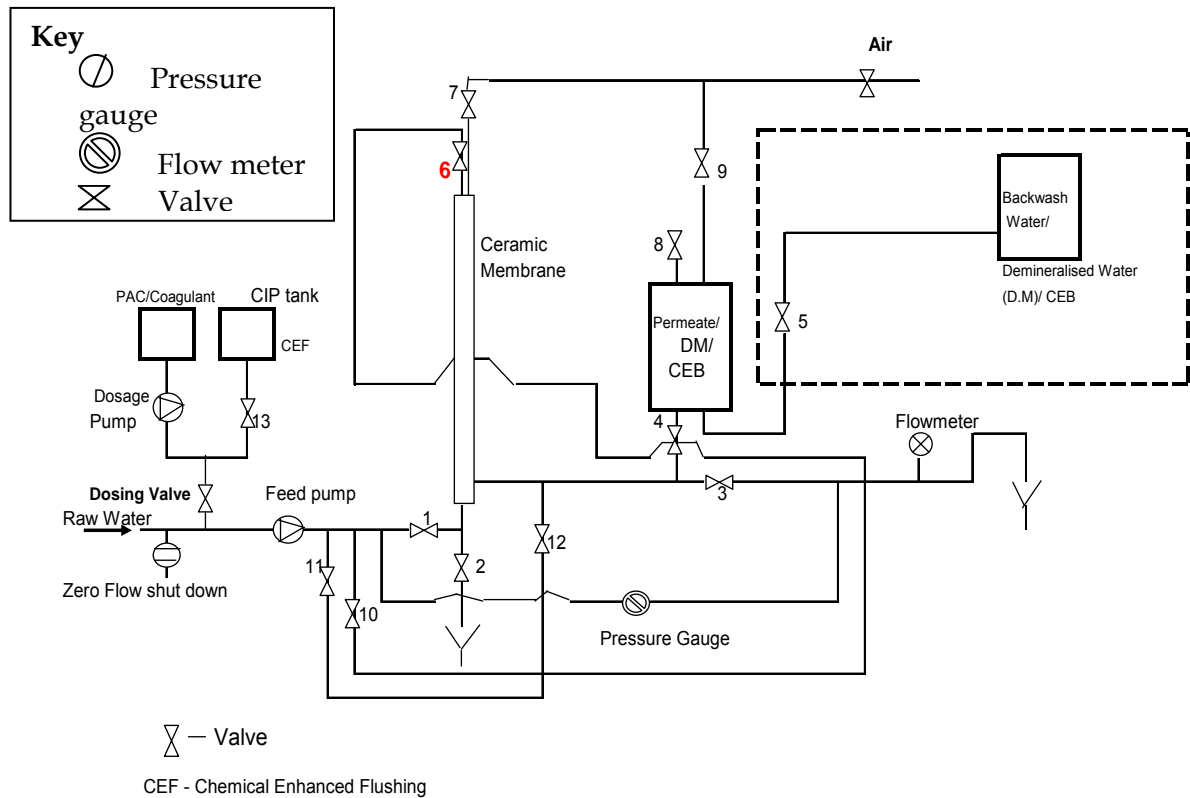


Figure 1: Schematic Layout of Pilot Plant (Ceramic)

2.5.2 Amicon (un) stirred Cell Set-up

Amicon (un) stirred cell is operated in a constant Pressure. To maintain the Flux the pressure has to be changed from time to time as the membrane fouled. The set-up of the equipment is shown below:-

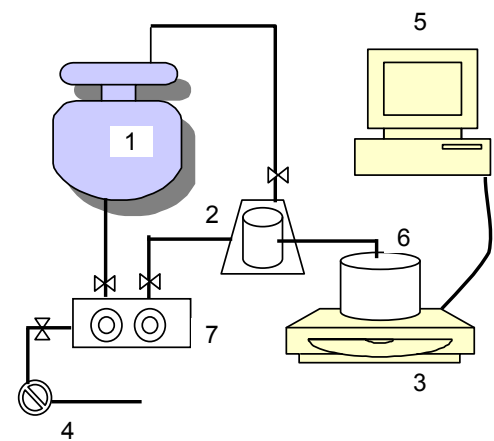


Picture

Figure 2: Amicon unstirred Cell

Key:

- 1 - Feed Reservoir, 2 - Stirrer Cell and Holder, 3 - Digital balance, 4 - Pressure sustaining valve, 5 - Computer, 6 - Filtrate vessel, 7 - Switch



Layout

2.6 Experimental Procedure

2.6.1 Pilot Plant – Ceramic membrane

Filtration

In automatic mode the filtration time for one cycle can be set accordingly (e.g 60 minutes). The Flux required is also set in terms of percentage where by 20% was equivalent to 150L/m².h flux when a membrane of 0.4m² cross-sectional areas is used. The data logger records automatically the flow, temperature, pressure and time for analysis. For filtration process valve no. 1 and 3 are opened and sometimes valve no 8 is also opened to release the air from backwashing vessel. Also dosing time was set to 4 minutes when a stock solution of S-PAC (7.5g/l) dosed at a rate of given rate (1.8 L/h).

However for adsorption experiments the pilot plant operated manual with dosing rate of 5L/h for few minutes depending on the number of layers that are required to be built.

Backwashing (BW)

During Filtration process in automatic mode, the backwashing vessel is started to be filled after 5 minutes. Valve no. 4 and 8 are opened and it takes about 10 minutes for the backwashing vessel to be filled but it depends upon the Flux used. The capacity of backwashing vessel is 5 Liters. For backwashing 2-3 Liters are enough that ensure that the vessel is not fully emptying to avoid interference of air in the system. The time set for backwashing was 16 seconds. Backwashing was done automatically after 1 hour of filtration cycle. The backwashing Flux was about 1,700L/m².h. The process of backwashing is started by opening of valve no. 10 so the water is bypassed and the pump can operate without being stopped. Valve 1 and 3 are closed and valve 2, 4 and 9 are opened. The backwashing process is a combination of water and compressed air (5bar). When the process is finished all valves are closed except valve 10 (Bypass).

Air Flushing (AF)

After backwashing the membrane is flushed automatically with compressed air (5 bars). The process is called Air Flushing. In this process normal all valves are closed except valve no. 2, 7 and 10 and it takes about 30 seconds for Flushing.

Forward Flushing (FF)

When Air Flushing is finished then the Forward Flushing is done automatically. The purpose of FF is to remove the remained air from the membrane that was left from AF process. In this process valve no. 10 is also closed and valve no 1 and 6 are opened. The Flush is done with high Flux of 300L/m².h and it takes about 1 minute. Then valve no.6 is closed and valve no. 3 is opened to start a new cycle.

Chemical Enhanced Backwashing (CEB)

CEB process was done by using 0.1M of NaOH and followed by 1% of Citric Acid. It was also done by using Sodium Hydroxide alone. The process was done on daily basis.

Chemical Cleaning

Chemical cleaning is employed to remove non-backwashable foulants in order to restore the function of membrane close to initial status in terms of permeability. The procedures involve soaking of membrane in 3000 ppm of Sodium Hypochlorite (NaOCl) solution at 20°C in a pH of 12 at least for 6 hours. Then the membrane is flushed with water to remove the Sodium hypochlorite before soaked again in Citric acid (1%) for at least 6 hours. The process was done once in a week.

2.6.2 Amicon Unstirrer Cell

The 0.1µm MF PVDF membrane cut into 58mm diameter size. The selection of PVDF membrane based on their pore sizes which is equivalent to ceramic membrane. With Amicon Cell (8200) the PVDF membranes are placed in a cell either single, double or triple depends on the initial flux required. The first step is washing the membrane with Milli Q water and membrane resistance can be also measured in this step by measuring the weight of the filtrate in a balance. The pressure is kept constant and with the Milli Q water filtration the Flux is almost remain constant.

The second step is addition of 180ml of S-PAC or N-PAC solution to the cell. In this experiment 70mg/l dose was selected. The pressure used in the first step filtration was also used in this step. The idea is to create the PAC pre-coat layer as well as to measure the PAC resistance. Therefore the filtrates are measured in a balance. The third step is filtration of raw water through pre-coat layers of S-PAC or N-PAC. Pre-filtered Delft water canal (with 0.45µm filters) was used.

Amicon un-stirrer cell is normal work at a constant Pressure. Therefore during filtration of Canal water through pre-coat layers of PAC, the flux declines as the PAC cake fouling increased. In order to keep at least average flux the pressure has to be adjusted from time to time. This can be possible done by monitoring the differences of filtrate weight in a balance. For good results at time interval of 30 seconds for recording of the filtrate weight is recommended.

2.7 Analytical Procedures for Measuring UV₂₅₄, DOC and Atrazine

UV absorbance machine was used to measure the absorbance intensity of the collected samples at the wavelength of 254nm. The unit of the absorbance is cm⁻¹. The DOC of raw water and the permeate samples were measured in a

TOC analyser. Machine can hold 60 samples in a time and it takes 15 minutes to measure one samples.

The atrazine content in water was measured by using the Atrazine ELISA (Microtiter Plate). The prepared samples are put together with standards in duplicate and the wavelength is set to 450nm. The procedures for preparation of samples are time consuming and need special care in order to have good results.



TOC Analyser



UV Spectrophotometer



Figure 3: Analytical Equipments

2.8 Modelling

The previous study in IHE by Ervin Orlandini (1995) on K and n values for atrazine removal from Milli Q water using activated carbon reveal that adsorption capacity K was 4.07 and adsorption intensity n was 0.25. These values have been adopted for modelling using STIMELA.

Similarly, another parameter for modelling that was remained unknown was mass transfer coefficient. This can be determined experimentally or by calculation based on filtration results of adsorptive filtration. The external mass transfer coefficient is the rate limiting controlling step in the systems that have:

- Poor mixing
- Dilute concentration of the adsorbate
- Smaller particle sizes of adsorbent

- And high affinity of adsorbate to adsorbent

Therefore, External mass transfer coefficient is regarded as a rate limiting controlling step when it comes to case of S-PAC pre-coat and atrazine removal. Therefore in modelling with STIMELA the internal mass transfer coefficient was also neglected. Ervin Orlandini (1999) in his study on Pesticide Removal by combined Ozonation and Granular Activated Carbon Filtration came up with the coefficient values of 15×10^{-04} cm/s (0.054m/h) and 9.6×10^{-13} cm²/s for external mass transfer coefficient (K_f) and effective surface diffusivity (D_s) respectively when virgin GAC was used.

When the particle sizes becomes very small, then the value of internal mass transfer coefficient becomes negligible, thus the Mass Transfer Coefficient becomes a product of external mass transfer coefficient and specific surface area of adsorbent.

$$K_2 = K_f \times a, \text{ where } a = \text{external surface area per unit particle volume} \\ = 3/R \text{ for the spherical particles of radius } R$$

and $R = d_1/2$, d_1 is particle diameter of adsorbent, therefore if consider porosity Mass transfer coefficient can be defined as:

$$K_2 = \frac{6K_f}{d_1(1-\varepsilon)}$$

Excel spread sheet has been employed to simplify the calculations as shown in *Appendix 1*:

3.0 Results and Discussion

3.1 Comparison of DOC, UV₂₅₄ and Atrazine Removal with Pre-coat Layer of S-PAC and N-PAC

The pore size of MF Ceramic membrane is 0.1 μ m and therefore NOM and SOCs can not easily be removed without pre-treatment (Seo *et al.*, 1997). Therefore the addition of powdered adsorbent to the membrane filtration influent is a simple and cost effective way to reduce NOM and SOCs in water (Matsui *et al.*, 2005)

The filtration of surface water containing NOM and SOCs through activated carbon filters (GAC) is subjected to two main mechanisms: preloading and competitive adsorption. NOM adsorption rates are mostly much lower than SOCs adsorption rates. Therefore, NOM moves faster through the GAC column whereby pre-adsorption of the NOM takes place in the lower part of the filter bed. Such kind of adsorption is known preloading with NOM (Orlandini, 1999).

Another mechanism which is taking place is competitive adsorption. Competitive adsorption is a process in which two or more adsorbates compete for the available adsorption sites. Competitive adsorption between NOM and Synthetic Organic Compounds (SOCs) may reduce the activated carbon adsorption capacity for SOCs (Upadhyaya, 1995). The presence of NOM in surface water is more than 100 times compared with SOCs (Orlandini, 1999). Therefore under competition adsorption SOCs is mostly like to suffer than NOM.

In MF membrane system associated with PAC pre-coat layers the effect of preloading is considered to be negligible since the layers are replaced after backwashing before starting a new filtration cycle. Therefore the only mechanism that will take place in a thin layer is competitive adsorption.

3.1.1 Removal of DOC, UV₂₅₄ and Atrazine without Competition

Pre-filtered Delft water canal was used to compare the removal of DOC and UV₂₅₄ by creating a pre-coat layer with a bed volume of 0.025cm³ that is equivalent to 70mg/l of S-PAC and N-PAC. Operational conditions are shown below:

	<i>S-PAC</i>	<i>N-PAC</i>
Average Flux (L/m².h)	145	145
No. of MF PVDF filters	2	2
Initial Pressure (bar)	0.2	0.15
Equivalent no. of Layers with 70mg/l	48	7

The same bed volume (0.025cm³) of S-PAC - (48 layers) and N-PAC - (7 layers) used in filtration of delft water canal (see Appendix 2). For atrazine removal, atrazine (0.1 mg/l) was dosed in Milli Q water to determine the removal efficiency of atrazine with S-PAC and N-PAC at the same bed volume (0.025cm³). An average flux of 145L/m².h and 170L/m².h was maintained for DOC/UV and atrazine experiments respectively. Samples were taken from to time to time. DOC, UV₂₅₄ and atrazine were measured. The results are shown below:

Table 4: DOC and UV₂₅₄ measurements of filtered Delft Canal water through S-PAC and N-PAC pre-coat layers over 0.1um PVDF membrane at Average Flux of 145 L/m².h

i) DOC and UV Removal

S-PAC						N-PAC				
Time (Min.)	DOC (mg/l)	UV ₂₅₄ (cm ⁻¹)	%DOC Removal	%UV Removal	SUVA (L/mg-m ⁻¹)	DOC (mg/l)	UV ₂₅₄ (cm ⁻¹)	%DOC Removal	%UV Removal	SUVA (L/mg-m ⁻¹)
0	1.64	0.053	91.6%	89.1%	3.23	2.81	0.074	85.6%	84.8%	2.63
5	5.87	0.129	69.9%	73.5%	2.20	9.56	0.218	51.0%	55.1%	2.28
10	6.55	0.162	66.4%	66.7%	2.47	12.05	0.283	38.2%	41.8%	2.35
15	9.27	0.207	52.5%	57.4%	2.23	13.31	0.32	31.7%	34.2%	2.40
20	9.97	0.234	48.9%	51.9%	2.35	13.96	0.345	28.4%	29.0%	2.47
30	12.82	0.301	34.3%	38.1%	2.35	14.72	0.38	24.5%	21.8%	2.58
45	14.55	0.368	25.4%	24.3%	2.53	15.9	0.414	18.5%	14.8%	2.60
60	14.98	0.399	23.2%	17.9%	2.66	17.42	0.429	10.7%	11.7%	2.46
75	15.90	0.416	18.5%	14.4%	2.62	17.55	0.437	10.0%	10.1%	2.49
90	17.40	0.427	10.8%	12.1%	2.45	18.8	0.446	3.6%	8.2%	2.37
105	17.51	0.434	10.2%	10.7%	2.48	18.92	0.451	3.0%	7.2%	2.38
120	18.76	0.438	3.8%	9.9%	2.33	18.92	0.451	3.0%	7.2%	2.38
					2.5					2.5
	19.50	0.486		Pre-filtered feed water		19.5	0.486			

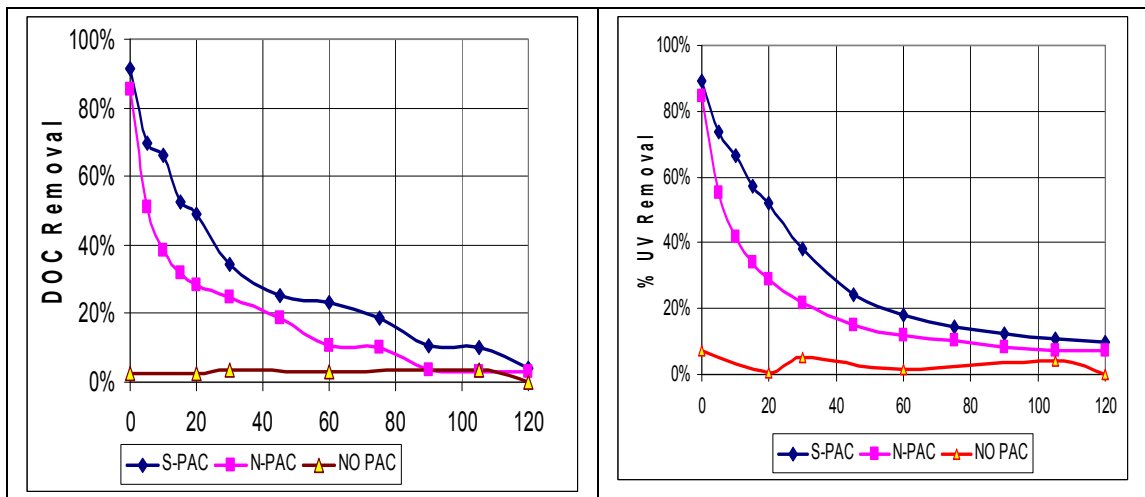


Figure 4: DOC and UV₂₅₄ Removals from filtered Delft Canal water through S-PAC and N-PAC pre-coat layers over 0.1um PVDF membrane at average flux of 145 L/m².h

Table 5: Summary of DOC and UV Removal with S-PAC and N-PAC

Time	DOC Removal - SPAC	DOC Removal - NPAC	UV ₂₅₄ Removal - SPAC	UV ₂₅₄ Removal - NPAC	SUVA (L/mg-m) S-PAC	SUVA (L/mg-m) N-PAC
20	49%	28%	50%	29%	2.35	2.47
45	25%	18%	24%	15%	2.53	2.6
60	23%	10%	18%	12%	2.66	2.46
90	10%	4%	12%	8%	2.45	2.37

NB: SUVA value for raw water = 2.5 L/gm-m

The results DOC and UV₂₅₄ removal from pre-filtered Delft canal water without PAC shows that the removal is ranging between 3-5% which is suggesting that MF membrane alone can not remove NOM. On the other hand, better DOC and UV₂₅₄ removal was observed with S-PAC than N-PAC. Results (Table 5 and Fig. 4) show that after 20 minutes of filtration DOC was 49% with S-PAC compared to 28% N-PAC. The same removal efficiency was observed in UV₂₅₄ removal. At recommended time of backwashing (45 minutes), the removal of DOC was 25% with S-PAC and 18% with N-PAC. S-PAC was exhausted after 90 minutes while N-PAC exhausted after 60 minutes of filtration.

The specific UV Absorbance (SUVA) is also used to classify the dominant group of DOC components. If $SUVA \leq 2$ L/mg-m non-humic NOM (e.g polysaccharides and proteins) is most likely to be a dominant group in raw water. When $SUVA \geq 4$ L/mg-m, then the raw water is rich in humic substances (Amy, 2006). The values of SUVA for raw water and permeate for Delft canal water after filtration through S-PAC and N-PAC were ranging between 2.33 - 2.7 suggesting that both raw and permeates are composed of both humic and non-humic substances. The value of SUVA after S-PAC filtration in the first 20 minutes was lowered from 2.5 to 2.35 suggesting that hydrophobics were better removed than hydrophilics (non-humic). Also, initially SUVA value rise to 3.23 from 2.5 suggesting that rapid removal of biopolymers (polysaccharides) compounds and thereafter SUVA decline as humic fraction is also removed. The same story was observed for N-PAC initially when SUVA value rise indicates that biopolymers are removed but the value is less compared with S-PAC. Also, the SUVA value declines from 2.5 to 2.47 showing low removal of hydrophobics (humic) in the first 20 minutes.

The hydrophobic fraction represents almost 50% of DOC with larger molecular weight while hydrophilic fraction is composed of 25-40% of DOC with lower molecular weight and their are commonly known as non-humic substances. The transphilic fraction is comprised with approximately 25% of DOC and its molecular weight ranged between hydrophobic and hydrophilic fractions (Tobar, 2007). Therefore, when S-PAC DOC up taking rate is compared to N-PAC then particle size is likely to influence the adsorption rate.

The particle sizes of S-PAC are roughly smaller than N-PAC, thus having large surface area which means more adsorption sites. The research done by (Matsui *et al.*, 2005) concluded that S-PAC removed NOM better than normal PAC did, owing to improvements in both adsorption kinetics and capacity. However there is a different opinion regarding the capacity of activated carbon from (Armenate, 2007).

The study by (Armenate, 2007) described the total surface area of the activated carbon used for adsorption to be not significantly affected by the particle size since micropore structure responsible for adsorption does not change despite the change of particle size (Armenate, 2007). This means that the adsorption capacities of small and large particles are not much different although the time required to achieve equilibrium can vary significantly because of the diffusion effects. The finer the particles mean equilibrium will be reached faster. While it needs one day for PAC to reach equilibrium GAC needs several days (Schippers *et al.*, 2007a)

Another study by (Najim *et al.*, 1990) insisted that the use of smaller particles provide faster adsorption kinetics. Therefore, when we referred to those studies we can suggest that capacity has significant importance when it comes to the question of comparing the different adsorbents and not the particle sizes of the adsorbent itself but the particle size is mostly affected by adsorption kinetics. The time taken by N-PAC to reach exhaustion is shorter (30 minutes less) than S-PAC, therefore this shows that the S-PAC has high capacity than N-PAC as observed by (Matsui *et al.*, 2005).

In general the results show that S-PAC and N-PAC in the form of pre-coat can be applied to remove NOM then the use of membrane alone. This is also was found by (Tomaszewska and Mozia, 2002) when they find that PAC/UF was very effective in removal of Humic Acid (HA) to 90% compared with UF alone (40%) when 100mg/l continuous dosing was used.

Conclusion:

The removal of DOC and UV₂₅₄ is much effective in the first 20 minutes with 50% for S-PAC and 28% for N-PAC. S-PAC exhausted after 90 minutes while N-PAC exhausted after 60 minutes (S-PAC is better in kinetic).

ii) Atrazine Removal

Atrazine (100µg/l) was dosed in Milli Q water to determine the removal efficiency of atrazine with S-PAC (48 layers) and N-PAC (7 layers) at the same bed volume (0.025cm³). An average flux of 170L/m².h was maintained. Samples were taken from to time to time. DOC, UV₂₅₄ and atrazine were measured. The results are shown below:

Table 6: Removal of Atrazine from Milli Q water through pre-coat layers of S-PAC (48 layers) and N-PAC (7 layers) over 0.1um MF PVDF membrane at Flux of 170L/m².h

S-PAC		%	N-PAC	%
Time (Min.)	Conc. (µg/l)	(Co-C)/Co	Conc. (µg/l)	(Co-C)/Co
0	0.40	99.6%	1.11	98.9%
5	0.48	99.5%	1.33	98.7%
10	0.89	99.1%	1.67	98.3%
20	2.00	98.0%	6.67	93.3%
30	0.11	98.9%	21.11	78.9%
60	0.20	98.0%		
Raw	100		100	

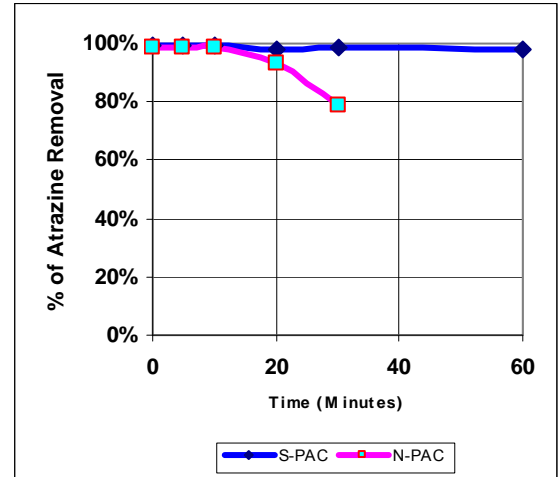


Figure 5: Removal of Atrazine from Milli Q water through pre-coat layers of S-PAC (48 layers) and N-PAC (7 layers) over 0.1um MF PVDF membrane at Flux of 170L/m².h

The Table 6 and figure 5 above showed that the removal of atrazine maintained to 98% with S-PAC pre-coat layers at the bed volume of 0.025cm³ during one hour of filtration. However for N-PAC when the same dose used the removal declined to 79% after 30 minutes. The breakthrough point (which is 10% of influent concentration) was not achieved for the case of S-PAC but it took 25 minutes for N-PAC. Therefore this shows that, when the same dose is applied for N-PAC and S-PAC for atrazine removal, without competitive adsorption then S-PAC show fast adsorption kinetics.

The removal efficiency of atrazine with S-PAC is comparable with the work published by (Tomaszewska and Mozia, 2002) on removal of phenol from distilled water using a combined PAC/UF process. The distilled water was dosed with 1mg/l of phenol and 10 mg/l of HA (Humic Acid). 50mg/l and 100mg/l of PAC were added continuously to the water as pre-treatment prior to UF membrane. The low flux of 40L/m².h was used. The permeate showed 98% and 100% removal of phenol for 50 and 100mg/l dose of PAC respectively. But despite using continuous dosing of PAC prior to UF membrane that have low molecular weight cut off than MF membrane in our case still we have achieved good removal of atrazine with just a pre-coat layer of S-PAC.

Conclusion:

S-PAC showed no breakthrough for S-PAC with respect to atrazine and a removal of 98% was achieved after one hour of filtration. In the case of N-PAC, breakthrough was achieved after 25minutes and the removal drop of 80% after 30 minutes of filtration.

3.1.2 Removal of UV₂₅₄ and Atrazine with Competitive adsorption

In real water, NOM is also present as well as pesticides such as atrazine. Competitive adsorption between atrazine and NOM may occur for adsorption site. A laboratory experiment was conducted to investigate the fate of atrazine in a competitive adsorption. Therefore atrazine was added to the pre-filtered delft canal water (with 0.45µm cellulose filters) to a concentration of 0.1mg/l. The delft water canal was then filtered on MF PVDF membrane (0.1 µm) through 0.025cm³ bed volumes of S-PAC dose and N-PAC dose respectively.

	S-PAC	N-PAC
Average Flux (L/m².h)	145	145
No. of MF PVDF filters	2	2
Initial Pressure (bar)	0.2	0.15
Equivalent no. of Layers with 70mg/l	48	7
Concentration of Atrazine (mg/l)	0.1	0.1

The results are summarized below:

Table 7: Removal of UV₂₅₄ with 70mg/l S-PAC and 70mg/l N-PAC pre-coat on 0.1µm MF PVDF membrane at average flux of 145L/m².h

S-PAC				N-PAC		
Time (Min.)	UV₂₅₄ (cm⁻¹)	UV/Vo	(UVo-UV)/UVo	UV₂₅₄ (cm-1)	UV/Vo	(UVo-UV)/UVo
0	0.05	0.09	91.3%	0.07	0.13	87.1%
10	0.16	0.31	68.8%	0.28	0.54	45.8%
20	0.22	0.43	57.5%	0.35	0.68	32.3%
30	0.27	0.51	49.0%	0.39	0.74	25.8%
45	0.33	0.64	36.3%	0.42	0.80	20.2%
60	0.38	0.73	26.9%	0.43	0.83	16.5%
90	0.43	0.82	17.7%	0.46	0.88	11.7%
120	0.45	0.86	13.7%	0.48	0.92	8.5%
Raw	0.52			0.52		

Table 8: Atrazine Removal with 70mg/l S-PAC and, 70mg/l N-PAC and without dose (Blank) by 0.1µm MF PVDF membrane at average flux of 145L/m².h

NO PAC				N-PAC				S-PAC			
Time (Minutes)	Conc. (µg/l)	(C/Co)	% (Co-C)/Co	Time (Min.)	Conc.(C)-µg/l	(C/Co)	% (Co-C)/Co	Conc.(C) -µg/l	(C/Co)	% (Co-C)/Co	
0	92	0.9	0.1	0	1.4	0.014	98.6%	1.55	0.016	98.5%	
15	93	0.9	0.1	10	35.0	0.350	65.0%	2.9	0.029	97.1%	
30	100	1.0	0.0	20	40.0	0.400	60.0%	10.5	0.105	89.5%	
45	100	1.0	0.0	30	40.0	0.400	60.0%	22.5	0.225	77.5%	
60	100	1.0	0.0	45	45.0	0.450	55.0%	30	0.300	70.0%	
75	100	1.0	0.0	60	45.0	0.450	55.0%	37.5	0.375	62.5%	
90	96	1.0	0.0	90	80.0	0.800	20.0%	70	0.700	30.0%	
120	93	0.93	0.1	120	80.0	0.800	20.0%	70	0.700	30.0%	
Raw	100										

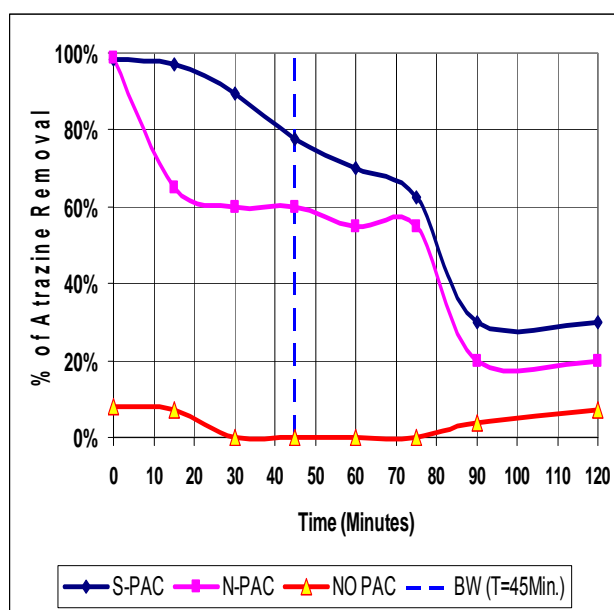


Figure 6: Atrazine Removal with 70mg/l S-PAC dose, 70mg/l N-PAC dose and without dose (Blank) by 0.1µm MF PVDF membrane at Average Flux of 145L/m².h

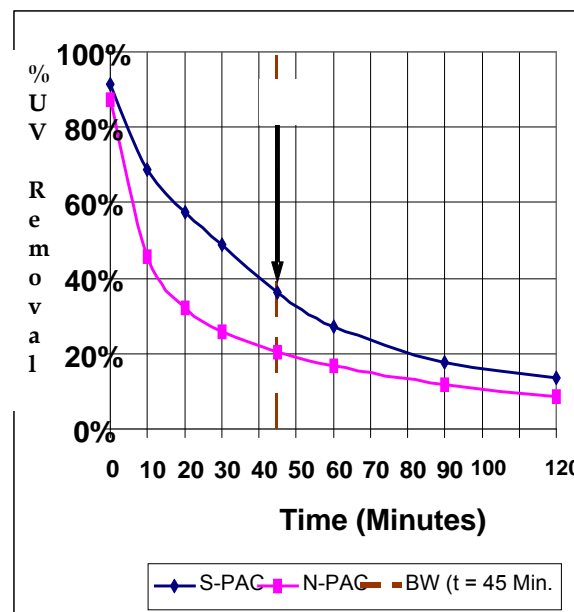


Figure 7: UV Removal with 70mg/l S-PAC dose and 70mg/l N-PAC dose by 0.1µm MF PVDF membrane at Average Flux of 145L/m².h

Where 45min is a time recommended for Backwashing. BW was not done actual it is only assumed.

Table 9: Summary of UV and Atrazine Removal with 70mg/l S-PAC, 70mg/l N-PAC dosed as pre-coat and Blank on a 0.1um MF PVDF membrane at average flux of 145L/m².h

Time	UV ₂₅₄ Removal -SPAC	UV ₂₅₄ Removal -NPAC	Atrazine Removal -70 mg/l SPAC	Atrazine Removal -70mg/l N-PAC
20	57 %	32 %	90 %	60 %
45	36 %	20 %	70 %	55 %
60	27 %	16 %	63 %	55 %
90	17 %	11 %	30 %	20 %

The blank experiment (without dose) shows almost no removal of atrazine this is suggesting that atrazine is removed by adsorption through S-PAC or N-PAC and can not be removed by membrane alone as explained by (Mozia and Tomaszewska, 2003) that MF and UF membrane can not remove NOM and SOCs without pre-treatment.

The results presented in table 9 shows that the removal of atrazine from canal water with S-PAC pre-coated on PVDF membrane was 90% and 63% after 20 and 60 minutes respectively. In case of N-PAC, the removal efficiency of atrazine was 60% and 55% after 20 and 60 minutes respectively. It was observed that there is a declining of the removal efficiency when compared with atrazine removal from Milli Q water that showed 99% and 93% for S-PAC and N-PAC respectively after 20 minutes. The decline in removal efficiency of atrazine from Delft water compared with Milli Q water is caused by competitive adsorption of NOM.

Assuming that a filtration cycle is 45 minutes (BW after 45 min.) and the pre-coat layer is refreshed from membrane after 45 minutes then 70% of atrazine can be removed with S-PAC from Delft canal water compared to 55% with N-PAC.

The breakthrough of atrazine removal with S-PAC observed after 20 minutes while N-PAC showed breakthrough after 3 minutes, and after 1 hour of filtration the adsorption sites started to become exhausted then atrazine probably is adsorbed in a preloaded PAC and its removal is dramatically reduced

Nevertheless, (Kennedy *et al.*, 2005) pointed that the performance of GAC on removal of pesticides depends on properties of natural organic matter (NOM) and not only the properties of pesticides alone.

Conclusions:

Atrazine removal was affected by presence of NOM in surface water and the removal decline from 98% to 70% with S-PAC. Removal efficiency of atrazine with S-PAC was still better (70% after 45 min.) compared with N-PAC (55% after 45 min.)

3.1.3 Comparison of Atrazine Removal in Milli Q water (no competitive adsorption) with S-PAC and N-PAC pre-coated in a 0.1µm MF PVDF membrane at different dose

0.1mg/l of atrazine was dosed in Milli Q water, and S-PAC layer of 20mg/l which is equivalent to 14 layers were used for adsorptive filtration. Milli Q was also filtered through 70mg/l of N-PAC dose (7 layers) which is equal to 0.025cm³ bed volumes. The results were compared with previous results filtration of Milli Q water through 70mg/l of S-PAC (48 layers). Atrazine removal was measured with ELISA kits. The results are shown below:

Table 10: Comparison of Atrazine Removal with 20mg/l and 70mg/l of S-PAC with 70mg/l of N-PAC through 0.1µm MF PVDF Membranes at Average Flux of 145L/m².h

S-PAC 70mg/l				S-PAC 20mg/l			N-PAC 70mg/l		
Time (Min.)	Conc. (µg/l)	% (Co-C)/Co	Time (Min.)	Conc.(C)-µg/l	(C/Co)	% (Co-C)/Co	Atrazine Conc. (C)	N-PAC (C/Co)	% (Co-C)/Co
0	0.4	99.6%	0	0.44	0.0044	99.6%	2.2	0.02	97.8%
5	0.5	99.5%	10	0.9	0.0090	99.1%	4.8	0.05	95.2%
10	0.9	99.1%	20	1.44	0.0144	98.6%	16.8	0.17	83.2%
20	2.0	98.0%	30	2.4	0.0240	97.6%	26.0	0.26	74.0%
30	1.1	98.9%	45	2.32	0.0232	97.7%	32.0	0.32	68.0%
60	2.0	98.0%	60	2.4	0.0240	97.6%	36.0	0.36	64.0%
Pre-filtered feed water	100		90	60	0.6000	40.0%	72.0	0.72	28.0%
			120	76	0.7600	24.0%	72.0	0.72	28.0%
			Pre-filtered feed water	100					

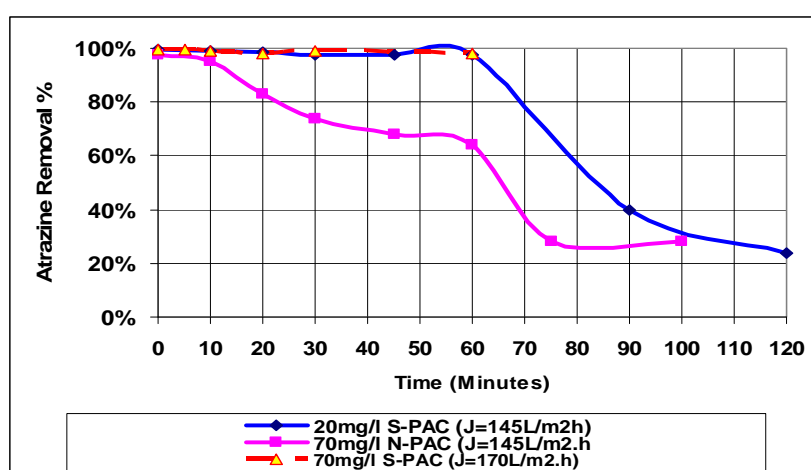


Figure 8: Comparison of Atrazine removal with 20mg/l and 70mg/l of S-PAC with 70mg/l of N-PAC through 0.1µm MF PVDF Membranes at average flux of 145L/m².h

The results in Table 10 and Fig. 8 shows that 98% removal of atrazine can be achieved for up to 1 hour of filtration with 70mg/l of S-PAC (48 layers) at a flux of 170L/m².h and 20 mg/l (14 layers) at a flux of 145L/m².h. Alternatively, the removal efficiency of atrazine was much lower only (62%) after 1 hour of filtration for 70mg/l of N-PAC (7 layers).

Breakthrough was achieved after 65 minutes with S-PAC (20mg/l) while N-PAC (70mg/l) showed breakthrough after 15 minutes. Thus, the dose of S-PAC can be a factor of 3 lower than N-PAC. This was also supported by (Matsui *et al.*, 2005) when he observed that NOM removal achieved with S-PAC at a dose of 5mg/l was not achieved by N-PAC even at a dose of 20 mg/l. (4 times higher).

Conclusions:

98% of atrazine was removed from Milli Q water with 20mg/l S-PAC while 65% of atrazine removal was achieved after 1 hour of filtration with 70mg/l N-PAC. Breakthrough achieved after 65 minutes with low dose of S-PAC (20mg/l) while N-PAC (70mg/l) took only 15 minutes.

3.1.4 Comparison of polymeric PVDF (0.1 μm) & Ceramic membrane ($\alpha\text{-Al}_2\text{O}_3$ 0.1 μm) pre-coated with S-PAC in terms of DOC & UV removal

A comparison between a polymeric PVDF membrane (flat sheet membrane tested in Amicon unstirred cell) and Ceramic membrane (a module with channels positioned upright) with S-PAC was performed on the basis similar number of pre-coat layers of S-PAC. The calculations shown in *Appendix 2* indicated 47 and 48 layers for Ceramic and PVDF membrane respectively. The average flux used was 150L/m².h. The delft water canal was used and filtrate samples were taken periodically. The DOC and UV₂₅₄ for influent and effluent were measured to determine the removal efficiencies as shown below:-

Table 11: DOC and UV₂₅₄ Removal with 48 Layers of S-PAC through 0.1um MF PVDF membrane and 47 Layers of 0.1 um MF Ceramic Membrane

MF PVDF Membrane					CERAMIC MEMBRANE - PILOT				
Time (Min.)	DOC (mg/l)	UV ₂₅₄ (cm ⁻¹)	% DOC Removal	% UV Removal	Time (Min.)	DOC (mg/l)	UV ₂₅₄ (cm ⁻¹)	% DOC Removal	% UV Removal
0	1.64	0.05	91.6%	89.1%	0	3.37	0.09	81.0%	84.1%
5	5.87	0.13	69.9%	73.5%	10	8.82	0.22	50.2%	62.0%
10	6.55	0.16	66.4%	66.7%	15	12.42	0.34	29.9%	39.6%
15	9.27	0.21	52.5%	57.4%	20	14.46	0.39	18.4%	30.9%
20	9.97	0.23	48.9%	51.9%	30	15.88	0.47	10.3%	17.0%
30	12.82	0.30	34.3%	38.1%	45	16.90	0.50	4.6%	11.5%
45	14.55	0.37	25.4%	24.3%	60	17.31	0.53	2.3%	6.5%
60	14.98	0.40	23.2%	17.9%	75	17.48	0.54	1.3%	4.2%
75	15.90	0.42	18.5%	14.4%	90	17.61	0.54	0.6%	4.6%
90	17.40	0.43	10.8%	12.1%	105	17.67	0.54	0.2%	4.6%
105	17.51	0.43	10.2%	10.7%	110	17.64	0.54	0.4%	5.3%
120	18.76	0.44	3.8%	9.9%	Pre-filtered feed water		17.71	0.57	
Pre-filtered feed water		19.50	0.49						

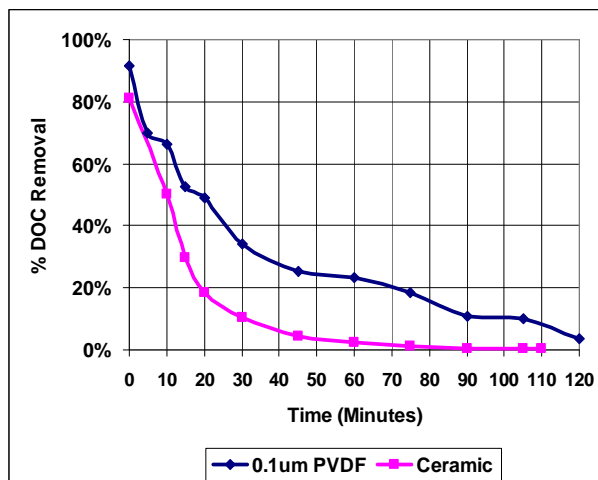


Figure 9: DOC Removal with 47 Layers of S-PAC over 0.1um PVDF membrane and 0.1 um Ceramic Membrane

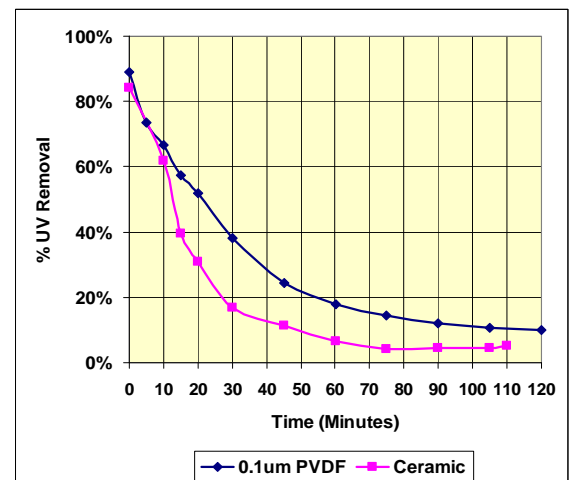


Figure 10: UV₂₅₄ Removal with 47 Layers of S-PAC on 0.1um PVDF membrane and 0.1 um Ceramic Membrane

The results shows that after 20 minutes of filtration PVDF membrane achieved 50% removal for both DOC and UV, while ceramic membrane achieved 20% removal for DOC and 30% removal of UV (Table 11, Fig. 9 and Fig. 10). The pre-coat layer of S-PAC in the ceramic membrane was exhausted (10% removal) after 30 minutes and 50 minutes respectively for DOC and UV removal, while DOC and UV removal with PVDF membrane exhausted after 90 minutes.

The PVDF membrane shows better results than ceramic membrane. Possible reason for low removal in ceramic is poor dispersion of the PAC layers inside the Ceramic membrane module. The second reason may be some of the PAC remained in suspension and did not take part in the pre-coat. This is because not all the water was emptied before filtration as in the case of PVDF membrane where the pre-coat layer was completely created by drying the suspension with pressure vessel.

The orientation and configuration of ceramic module make the task of distributing the PAC layers evenly through the tubular ceramic channels to be more difficult compared with the flat sheet membranes like PVDF and ceramic membrane. While the PVDF membrane was placed horizontal in the Amicon unstirred cell, ceramic membrane was oriented vertical, and this may affect the distribution of PAC as the two forces gravitational and hydraulic pressure are meet together.

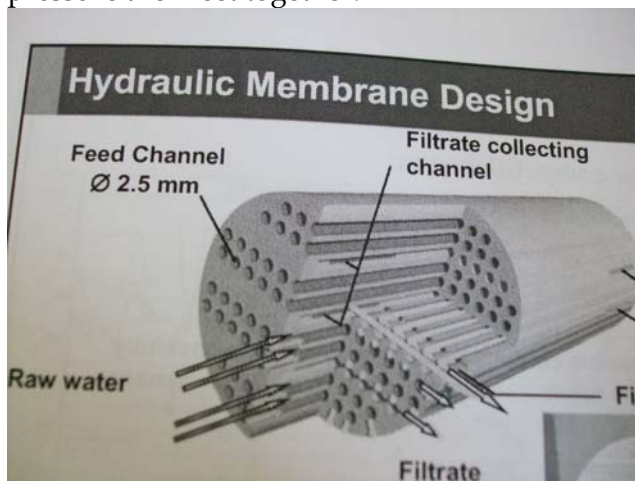


Figure 11: Ceramic Membrane Module (Interior structure) Figure 12: Used MF PVDF membrane covered with S-PAC

Conclusions:

After 20 minutes, 50% removal was achieved with PVDF membrane for both DOC and UV₂₅₄ while ceramic membrane achieved 20% removal for DOC and 30% removal of UV₂₅₄. S-PAC in ceramic membrane exhausted after 30 minutes (DOC) and 50 minutes (UV) respectively while with PVDF membrane exhausted after 90 minutes.

3.1.5 PAC Cake Fouling

A batch experiment was carried out to determine the impact of NOM adsorption on S-PAC, N-PAC and the PVDF membrane. Pre-filtered (through 0.45 μ m Filter) Delft canal water was used for all 3 experiments. The dose of S-PAC and N-PAC used was 70mg/l and the starting pressure was 0.2 bars. Single, double and triple filters were used for S-PAC, N-PAC and blank respectively. The reason was to control flux in order to create average operating conditions.

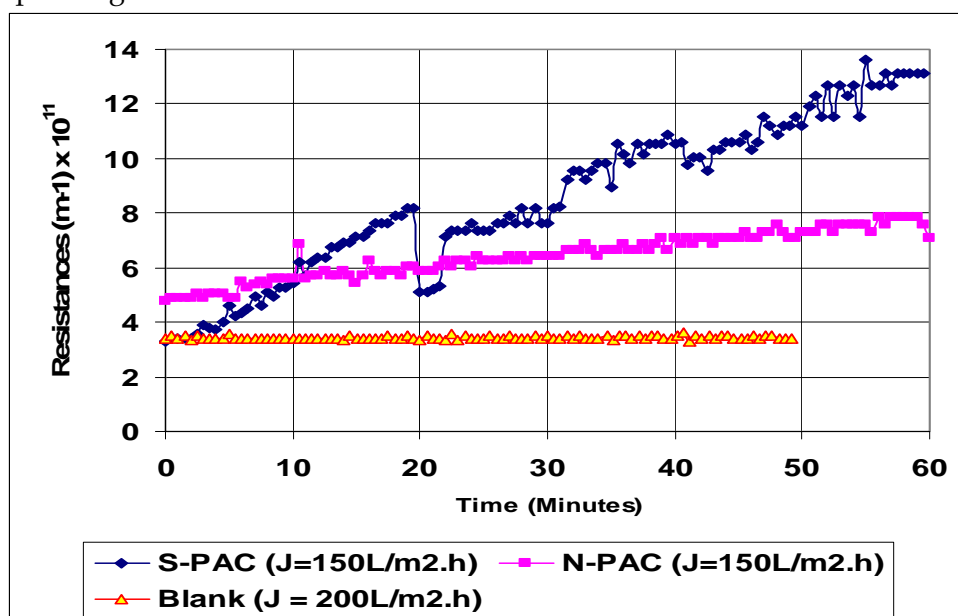


Figure 13: Resistances of 0.1 μ m PVDF membrane with S-PAC, N-PAC pre-coat layers and Blank membrane at average flux of 150L/m².h

The initial pressure at the beginning of experiment was 0.2 bars for all experiments. There was no increase on pressure for pre-filtered canal water with the MF PVDF membrane. The DOC removal for the blank was 5% indicates the fouling is slowly taking place. However the pressure of 0.2 bars is little bit high so it is difficult to notice the increase of resistances especial in the beginning of experiment. Therefore the resistance remained constant as shown in figure 13.

It was observed that when raw water filtered through 70mg/l N-PAC pre-coat layer, the resistance increase from 4.5 to 7 x 10¹¹ m⁻¹ after 1 hour of filtration with average Flux of 150 L/m².h. But the filtration of raw water through 70mg/l of S-PAC shows different phenomena. The resistance rise from 2.7 to 13.5 x 10¹¹ m⁻¹ after 1 hour of filtration as shown by the figure 13 above.

PAC Cake Fouling may occur through adsorption of NOM, particulates and metal ions (Zhao *et al.*, 2005). PAC may forms a cake layer combined with colloids, metals and NOM, providing an adsorption zone for further removal of NOM or hydraulic resistance layer to permeation (Zhao *et al.*, 2005). All three constituents can take part simultaneously or individually.

Particulates are assumed to be negligible since the water was pre-filtered by using 0.45µm that removes turbidity as well as some of organic matter. Metal ions that were dominant in Delft water canal are Calcium and Magnesium that were found in the range of 120 – 140 mg/l for Ca and 25 mg/l for Mg (Kamanyi, 2006). But the notable metal ion that may highly contribute to PAC fouling is Iron II when oxidized to Iron III (Zhao *et al.*, 2005). However Iron II is not expected in surface water in aerobic conditions and most of the iron in the canal water is already present in Fe³⁺ form (Schippers *et al.*, 2007a). Therefore, what is remaining is NOM that is adsorbed in PAC and form PAC cake fouling.

The results shows high increase rate of resistances for S-PAC compared with N-PAC and blank experiment which however, showed slightly increase of resistances which almost constant which strongly support that MF membranes can not remove NOM without pre-treatment.

Conclusions:

The rapid rise of resistance of filtration through S-PAC layer compared with N-PAC layer. This is suggesting that there a resistant layer is formed by either the adsorbed NOM or strained NOM. Blank test results showed that NOM without pre-treatment is not removed with Ceramic or PVDF membrane alone.

3.1.6 LC-OCD Test for filtrate of S-PAC and N-PAC

The samples from adsorptive filtration of S-PAC and N-PAC were further analysed to determine the fate of NOM components on adsorption. The samples were taken at interval of 15 minutes for a period of 1 hour. Therefore, 5 samples of S-PAC and N-PAC each were analysed in Harlem laboratory. The results are shown by the following tables and graphs.

Table 12: Composition of Delft Canal Water (NOM Fractions)

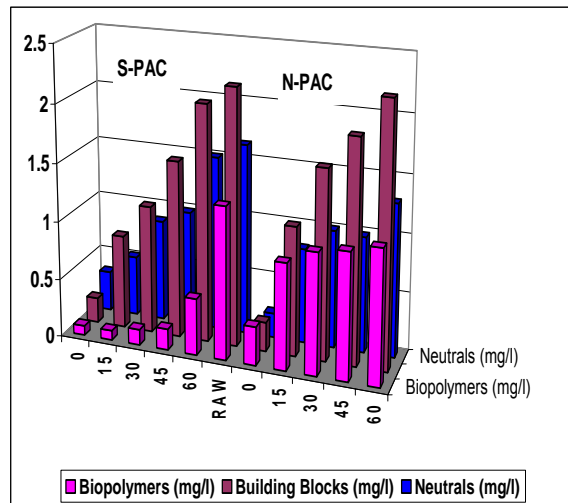
DOC (MG/L)	BIOPOLYMERS	HUMIC SUBSTANCE (HS)	BUILDING BLOCKS	NEUTRALS	LMW ACIDS
15.4	8.4%	66.7%	14.2%	10.6%	0.1%
mwco	> 20,000 Da	1,000–20,000 Da	300-500 Da	< 350 Da	< 350 Da

The composition of Delft water Canal is mainly composed with Humic substances that are contributing to 2/3 of NOM fractions as shown in Table 12.

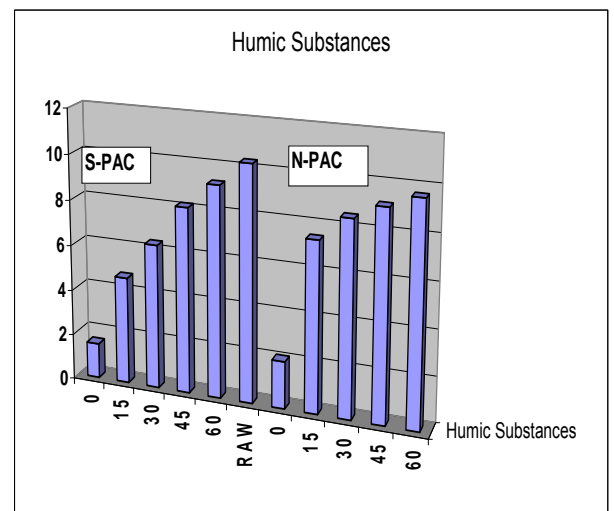
Table 13: DOC Fractions for permeates filtered through pre-coated layers of S-PAC & N-PAC at Flux of 145L/m².h with MF PVDF membrane

Sample	Biopolymers (mg/l)	HS (mg/l)	Building Blocks (mg/l)	Neutrals (mg/l)	Acids (mg/l)
S1 (t = 0)	0.081	1.543	0.215	0.345	0
S2 (t =15)	0.082	4.71	0.806	0.519	0.008
S3 (t = 30)	0.135	6.344	1.099	0.876	0.018
S4 (t = 45)	0.182	8.142	1.521	0.989	0
S5 (t = 60)	0.483	9.255	2.031	1.502	0.06
RAW	1.299	10.299	2.195	1.639	0
N1 (t = 0)	0.329	2.071	0.25	0.211	0.007
N2 (t =15)	0.904	7.442	1.102	0.813	0.098
N3 (t = 30)	1.028	8.501	1.617	1.006	0.159
N4 (t = 45)	1.071	9.122	1.9	0.989	0
N5 (t = 60)	1.137	9.649	2.231	1.305	0

The detailed results are shown in *Appendix 3*



a.



b.

Figure 14: DOC Fractions of permeates of Delft Water Canal filtered in pre-coated MF PVDF membrane with S-PAC and N-PAC respectively. (a) Biopolymers, Building Blocks and Neutrals (b) Humic Substances (HS)

Table 14: Fractions of NOM

Fraction categories	Definition
Humics (HS)	Humic and Fulvic Acids (1,000 - 20,000 Da)
Building Blocks	Weathering and oxidation products of Humics (300 - 500 Da)
Low molecular Weight (LMW) organic Acids	Aliphatic low molecular weight organic acids (< 350 Da)
LMW Neutrals	Alcohol, Aldehydes, ketones (< 350 Da)
Biopolymers	Associated with peptides or proteins and originated from algae and bacteria (> 20,000 Da)

Source (Kennedy *et al.*, 2005)

100,000 Da \approx 10 nm

Pore sizes of PAC/GAC

< 2 nm micropore

> 50 nm macropore

2 - 50 nm mesopore

Figure 14 showed S-PAC removed > 80% of biopolymers after 45 minutes of filtration compared with 20% removal by N-PAC at the same time. Also, S-PAC removed 40% of Humic substance (H.S) after 30 min while N-PAC removed only 20% of H.S (after 30 min.). Humic substances have a wide range of molecular weight cut off (mwco) but also contribute to 2/3 of the NOM fractions that made to be a major cause of fouling in case of canal water.

The removal of Building blocks by S-PAC is 50% after 30 minutes which is better than N-PAC removal of 30% after 30 minutes. However, both S-PAC and N-PAC achieved 40% removal of neutrals after 45 minutes of filtration. In general, Humic substances showed poor removal as well as building blocks. On regards of pore sizes, Biopolymers can only be removed by mesopore, therefore when the pore size is exhausted then this fraction starts to be resistant to removal. The bed porosity of S-PAC layer is 0.045 μ m (0.15d) that form straining which enable physical removal of biopolymers due to their large molecular weight than other NOM (> 0.002 μ m) and hence cause rapid increases of resistances in S-PAC.

Humics can be removed by micropores and mesopores and LMW and building blocks can be removed with micropore. Therefore when micropore is also exhausted LMW Acids, humics and building blocks are starting to suffer. N-PAC also showed good removal of biopolymers and LMW Acids in the first 15 minutes.

Conclusion:

LC-OCD test showed high removal of biopolymers (>80%) in the first 45 minutes with S-PAC which is influenced by physical removal with straining phenomena. Also LMW Acids were removed significantly in the first 30 minutes with poor removal of humics and building blocks after 15 minutes of adsorptive filtration.

3.2 Modelling

To predict of breakthrough of the adsorbent, models that make use of isotherm parameters, mass balance and mass transfer equations are employed. Therefore the linear driving force model (LDF) is applied to illustrate the adsorption of atrazine through S-PAC. Stimela software package developed by TU Delft, KIWA and DHV was applied.

Stimela was used to compare the Laboratory results of atrazine removal with S-PAC and N-PAC without competitive adsorption. The adsorption capacity (K) and adsorption intensity (n) for atrazine removal with GAC determined by Orlandini (1999) were adopted for modelling. It is assumed that there is no significant change on K and n values with variation of PAC particle sizes what is varying is the time to reach equilibrium (Armenate, 2007). Therefore, K value and n adopted are 7.14 and 0.18 respectively. Mass transfer coefficients as a function of unit time (K_2) was calculated for S-PAC is shown in *Appendix 1*. The effluent concentration was periodically measured and compared with influent.

3.2.1 Modelling Atrazine (0.1 mg/l) adsorption on 20mg/l S-PAC pre-coat layer through 0.1 μ m MF PVDF membrane

K_2 value was calculated based on effective size of 0.3 μ m of S-PAC as shown in *Appendix 1*. The data input for Stimela Modelling are shown below:

Stimela Online Dynamic				
Activated carbon filter - Laboratory				
No.	Input Parameter	Quantity	Unit	Remarks
1.	Filter run time	0.08	Days	
2.	Filter surface Area	0.00264	m ²	
3.	Bed height	0.00001	m	
4.	Water Flow	0.00038	m ³ /h	
5.	Grain size	0.0003	mm	S-PAC Effective size
6.	Filter Porosity	50	%	
7.	Mass Density of Activated Carbon	500	Kg/m ³	
8.	Freundlich constant - n	0.18		
9.	Freundlich constant - K	7.14	(g/kg)*(m ³ /g) ⁿ	
10.	Mass Transfer Coefficient - K_2	4178864	h ⁻¹	K_2 calculations - see Appendix 1
11.	Completely Mixed reactor	1		

Table 15: Laboratory results for Atrazine Effluent (20mg/l S-PAC)

S-PAC - 20mg/l		
Time (minutes)	Atrazine Conc - C (mg/l)	C/C ₀
0	0.00044	0.0044
10	0.0009	0.009
20	0.00144	0.0144
30	0.0024	0.024
45	0.00232	0.0232
60	0.0024	0.024
90	0.06	0.6
120	0.076	0.76
Raw (C₀)	0.1	

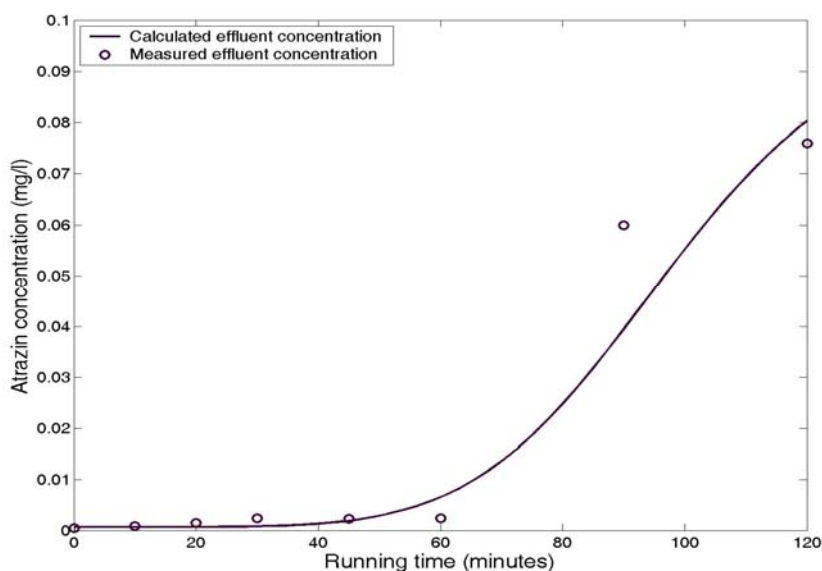


Figure 15: Laboratory and Modelling results of atrazine removal through S-PAC (20mg/l) with PVDF membrane at Average Flux of 145L/m².h

NB: The experimental data are shown in point form while Modelling results are shown by a curve (line)

Both laboratory results and modelling shows the breakthrough point after a 1 hour. The removal of atrazine after 2 hours from laboratory results was 24% and the model results shows 20% removal so it is quite similar. The difference is about 16% between the two value Both Model and Laboratory results shows that removal efficiency of more than 90% in the first hour of filtration

Conclusion:

Both laboratory and modelling results of atrazine removal with 20mg/l S-PAC in PVDF membrane shows breakthrough after a 1 hour

4.0 CONCLUSIONS

4.1 Adsorptive Filtration through S-PAC and N-PAC (70mg/l pre-coat layers with bed volumes of 0.025cm³)

- The breakthrough points ($C = 10\%C_0$) were just achieved within first 5 minutes of filtration. Also, 50% of DOC and UV_{254} removal was achieved after 20 minutes with S-PAC and 30% with N-PAC respectively S-PAC exhausted ($C = 90\%C_0$) after 90 minutes of Filtration while N-PAC exhausted after 60 minutes when a flux of 145L/m².h applied to the filtration of Delft water canal.
- The formation of PAC cake fouling was very rapid in S-PAC than in N-PAC. Total resistance of membrane increases from 3 to $13 \times 10^{11} \text{ m}^{-1}$ in case of S-PAC and from 4.5 to $7 \times 10^{11} \text{ m}^{-1}$ for N-PAC. The increase of resistance slope by S-PAC was 4 times more than N-PAC indicates high rate of adsorption of S-PAC and therefore can reduce membrane fouling more than N-PAC.
- Humics (HS) contribute to 2/3 of NOM in Delft water canal and is a major cause of fouling. Biopolymers and LMW Acids are major components that contribute to PAC cake layer fouling. The bed porosity of S-PAC is 0.045 μm (0.15d) suggesting that biopolymers are subject to physical removal by micro-straining formed by bed porosity of S-PAC. This might be the reason for rapid resistance increase when S-Pac pre-coat layer is used.
- Atrazine removal was maintained to 99% with 70mg/l of S-PAC after 1 hour and drop to 80% after 30 minutes with 70mg/l of N-PAC without NOM competition. No breakthrough achieved after 1 hour filtration through S-PAC but with N-PAC it was achieved after 25min. S-PAC (20mg/l) shows better removal of atrazine achieving 98% removal compared with 65% with 70mg/l of N-PAC without competition. 20mg/l of S-PAC achieve breakthrough after 1 hour of filtration.
- Atrazine removal is affected by NOM as both compete for the available adsorption sites. Atrazine removal drop from 99% (without competition) to 62% (with competition) after 1 hour of filtration with 70mg/l of S-PAC, and drop to 55% (under competition) from 65% (without competition) after 1 hour of filtration with 70mg/l N-PAC (pre-coat layers).
- Breakthrough point for Atrazine removal (under competition) was achieved after 20 minutes with 70mg/l of S-PAC and took about 5 minutes with the same dose of N-PAC. The adsorption of atrazine is affected by competition with NOM but atrazine has a negligible effect on DOC and UV_{254} removal since its concentration is very low.

- PVDF membrane with 48 layers of S-PAC shows better removal results on DOC and UV₂₅₄ than ceramic membrane with 47 layers of S-PAC at a Flux of 150L/m².h. DOC and UV₂₅₄ removal with S-PAC in ceramic membrane exhausted after 30 minutes and 50 minutes respectively while with PVDF membrane exhausted after 90 minutes. PVDF membrane achieves 50% removal of DOC and UV₂₅₄ after 20 minutes while ceramic membrane achieves 20% removal of DOC and 30% removal of UV₂₅₄. This is suggesting that PAC layers were not well dispersed in Ceramic membrane channels.

4.2 Modelling

- The laboratory results shows similar trend with Modelling for S-PAC with breakthrough point achieved after 1 hour. Therefore it is economical to use finer particles and refreshed by the new pre-coat layer after 1 hour of filtration
- Stimela Model is promising a chance for prediction of breakthrough curve behaviour for S-PAC; however more laboratory experiments are required to validate the statement.

General Conclusion:

S-PAC showed better removal efficiency for atrazine, DOC & UV₂₅₄ in both situations (with and without competition) at the same dose and lower dose than N-PAC

5.0 References

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6.0 APPENDICES

Appendix 1

EXTERNAL MASS TRANSFER COEFFICIENT (Kf)

DATA INPUT

Porosity (PAC) - ϵ	0.5	
Membrane Diameter (d)	0.058	m
Average Flow - Q	0.38	L/h
Density of water ρ	1000	kg/m ³
Temperature of water (T)	20	°C
Association parameter for Water (X)	2.6	
Molecular wt of Water (M)	18	g/mole
Molar Mass of atrazine (m)	215.685	g/mole
Density of atrazine (ρ_a)	1.187	g/cm ³
Particle diameter - d_1	0.0003	mm

DATA OUTPUT

Dynamic viscosity (μ)	0.00100586	
Kinematic Viscosity (ν)	1.0059E-06	
Radius of membrane filter - R	0.029	m
Average flow in m ³ /s - Q	1.0556E-07	m ³ /s
Membrane Area - A	0.00264314	m ²
Filtrate Velocity (V)	3.9936E-05	m/s
Molar volume of atrazine (Vb)	181.705981	g/cm ³
Diffusivity of Atrazine (D_{AB})	6.5023E-06	cm ² /s
Reynolds Number - Re	2.30	OK
	(0.0016 < Re < 55)	
Schmidt Number - Sc	1.55E+03	OK
	(165 < Sc < 70,600)	
Sherwood Number - Sh	2589	
External Mass Transfer Coefficient - K_f	0.10	m/h

$$\mu = \frac{497 \times 10^{-3}}{(T + 42.5)^{1.5}}$$

$$\nu = \frac{\mu}{\rho}$$

d/2

$$A = \pi d^2/4$$

$$V = Q/A$$

$$V_b = m/\rho_a$$

$$D_{AB} = 7.4 * 10^{-11} \frac{(XM)^{0.5} (T + 273)}{\mu V_b^{0.6}}$$

$$Re = \frac{2RV}{\nu}$$

$$Sc = \frac{\nu}{D_{AB}}$$

$$Sh = \frac{1.09(Re.Sc)^{1/3}}{\epsilon}$$

$$K_f = \frac{Sh \cdot D_{AB}}{2R}$$

MASS COEFFICIENT (K2)

Mass Transfer Coefficient - K_2

4,178,864 1/h

$$K_2 = \frac{6 K_f}{d_1 (1 - \epsilon)}$$

Appendix 2

Number of layers formed in S & N-PAC pre-coat

Submicron Powder activated carbon (S-PAC) with effective size of $0.3\mu\text{m}$ and Normal Powder activated carbon (N-PAC) with effective size of $2\mu\text{m}$ was used to form pre-coat layers. 180ml of PAC solutions containing 70mg/l of S-PAC and N-PAC each were filtered through $0.1\mu\text{m}$ PVDF membrane placed Amicon unstirred cell until it is completely dry at constant pressure of 0.2bars. The layers of S-PAC or N-PAC containing 12.6mg or 0.025cm^3 are formed at the top of MF PVDF membrane. This is equivalent to 48 layers for S-PAC and 7 layers in case of N-PAC. The below calculations show the calculations procedures.

C). PVDF membrane

PAC (mg/l) - C	70	
Particle diam.(um) - d	0.3	
Volume Filtered (L) - Vf	0.18	
Density (g/cm^3) - ρ	0.5	
Weight of PAC (g) -M'	0.0126	$M'=C.Vf/1000$
Volume of PAC (cm^3) - Vb'	0.0252	$Vb'=M'/\rho$
Vol. of 1 particle (cm^3) - V_1	$1.41429\text{E}-14$	$V_1=\pi d^3/6$
Membrane Area - A_m	0.00264	m^2
Area of 1 particle - A_1 (m^2)	$7.07143\text{E}-14$	$A_1 = \pi d^2$
No. of particles for Monolayer - n	$3.73\text{E}+10$	$n = A_m/A_1$
No of particles in Vol. Filtered - N	$1.78182\text{E}+12$	$N=Vp'/V_1$
No. of layers - N_T	48	$N_T=N/n$

CALCULATIONS OF EMPTY BED CONTACT TIME (EBCT)

$$EBCT = Vb/Q$$

Where Vb = Carbon Bed
Volume, Q = Flow rate

and A = membrane
Area

$Vb = Vb' =$	0.0252 cm^3
Flux - J	$180 (\text{L}/\text{m}^2.\text{h})$
Membrane Area - A_m	0.00264 m^2
Flow - $Q = J*A_m$	0.4752 l/h
EBCT	$5.30\text{E}-05 \text{ Hours}$

Therefore Contact Time (Seconds)	EBCT	0.19 Seconds
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B). CERAMIC MEMBRANE WITH REDUCED AREA

Stock Solution (mg/l)	7,500	Ct	
Dosing rate (l/h)	5	q	
Feed Rate (Raw water) - Q in l/h	19.65	Q	
Total Flow $Q_T = Q + q$	24.65	Q_T	
PAC (mg/l) - Do	1521.30	$Do = q \cdot Ct / Q_T$	t 2 Dosing time
Particle diam.(um) - d	0.3	d	
Volume Filtered (L) - V	0.66	$V = Q \cdot t$	Assume Dosage volume remained in membrane
Density (g/cc) - ρ	0.5	ρ	
Weight of PAC (g) - M	0.996	$M = Do \cdot V$	A (m ²) 0.131
Volume of PAC (cm ³) - Vp	1.993	$Vp = M / \rho$	J (l/m ² .h) 150
Total Volume in one channel (cm ³) - Vt	4.91	$Vt = (\pi D_c^2 / 4) \cdot L_m$	Q (l/h) 19.65
Total Volume of all channels in a module V_T - (cm ³)	88.39	$V_T = N \cdot V_t$	
Percentage of PAC in a Module (R') channels	2.25%	$R' = (V_p / V_T) \cdot 100\%$	

$Q = J/A$

Total Number of Particles in one layer:

Number of channels - N	18	N	Channel diam. (mm) - D_c	2.5 mm	Module length (m) - L_m	1
Diameter of channel remained after PAC coat layer		D_1				
% Percentage of channel remained after PAC dosing - R				97.75%	$R = 100 - R'$	
				0.977	R	

Relationship between number of particles along the centre of channel (N_c) is given by $N_c \cdot d = (D_c - D_1) / 2$..Eq.1 where d is particle diameter

If R is % of the channel that is not covered by PAC then,

Volume of remained channel $V_r = R \times V_t$ where V_t is a total Volume of a channel

$V_r = R \cdot V_t$ where V_t is a volume of channel

$\pi \cdot D_1^2 \cdot L_m / 4 = R \cdot \pi \cdot D_c^2 \cdot L_m / 4$

$D_1 = R^{1/2} \cdot D_c$ Equation 2

From Equation 1: $D_1 = D_c - 2N_c \cdot d$, therefore substitute D_1 in Equation 2

$D_c - 2N_c \cdot d = R^{1/2} \cdot D_c$

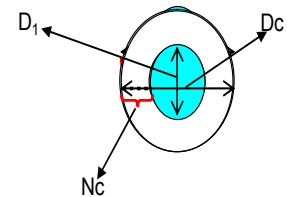
$N_c = (D_c - R^{1/2} \cdot D_c) / 2d = D_c(1 - R^{0.5}) / 2d$

N_c = number of layers formed in one channel after PAC dosing

Therefore Total number of Layers in a module (N_T) = $N_c \times N$

N_c	47.24	$D_c(1 - R^{0.5}) / 2d$
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Number of Layers - N	47
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CALCULATIONS OF EMPTY BED CONTACT TIME (EBCT)

EBCT = V_b / Q

Where V_b = Carbon Bed

Volume, Q = Flow rate

Q = J.A, J = Flux and A = membrane Area

$V_b = V_p =$	1.99 cm ³
Q =	20 l/h
EBCT	1.01E-04 Hours


Therefore Contact Time (Seconds)	EBCT	0.37 Seconds
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Table 16: Summary of Number of Layers of S-PAC and N-PAC over MF membrane (0.1 μ m) for different doses

MF PVDF (0.1 μ m)			Ceramic Membrane (0.1 μ m)	
Dose (mg/l)	Number of Layers (S-PAC)	Number of Layers (N-PAC)	Dosing time (Minutes)	Number of Layers (S-PAC)
20	14	2	1	9
50	34	5	2	17
70	48	7	3	26
100	68	10	5	43
150	102	15	10	87

Based on number of layers, filtration experiments using pre-filtered surface water and then Milli Q was done to compare the removal efficient of atrazine, DOC (mg/l) and UV₂₅₄ by using S-PAC and N-PAC.

Appendix 3: LC-OCD Tests for N-PAC & S-PAC permeates and Pre-filtered Delft Water Canal

Project: 0		Partitioning of Organic Carbon (OC)					Chromatographic Fractionation of Organic Carbon (CDOC)								(UV@254 nm)		
sampl.date	1/0/1900	Approx. Molecular Weights in g/mol: →					>>20,000	~1000 (see separate HS-Diagram)				300-500	<350	<350	Inorg. Colloid. SAC (m ⁻¹)	SUVA (SAC/OC) L/(mg*m)	
		TOC=DOC+POC	DOC=CDOC+HOC	Note: POC, hence TOC may be too low			Bio-Polymers	DON (Norg)	Humic Subst. (HS)	DON (Norg)	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Building Blocks	Neutrals			Acids
		total OC	dissolved	particul.	hydrophob.	hydrophil.	ppb-C	ppb-N	ppb-C	ppb-N	L/(mg*m)	g/mol	ppb-C	ppb-C	ppb-C		
		% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--	--
Sample S1		2241	2215	26	32	2183	81	5	1543	87	3.05	641	215	345	0	0.03	2.82
		100	98.8	1.2	1.4	97.4	3.6	--	68.8	--	--	--	9.6	15.4	0.0	--	--
Sample S2		6335	6297	38	172	6125	82	4	4710	348	3.65	605	806	519	8	0.04	3.18
		100	99.4	0.6	2.7	96.7	1.3	--	74.3	--	--	--	12.7	8.2	0.1	--	--
Sample S3		8802	8581	221	110	8471	135	11	6344	473	3.43	586	1099	876	18	0.12	3.17
		100	97.5	2.5	1.2	96.2	1.5	--	72.1	--	--	--	12.5	9.9	0.2	--	--
Sample S4		10995	10778	218	-56	10833	182	17	8142	352	3.90	608	1521	989	0	0.02	3.47
		100	98.0	2.0	-0.5	98.5	1.7	--	74.0	--	--	--	13.8	9.0	0.0	--	--
Sample S5		13710	13413	297	82	13331	483	48	9255	781	4.33	570	2031	1502	60	0.08	3.48
		100	97.8	2.2	0.6	97.2	3.5	--	67.5	--	--	--	14.8	11.0	0.4	--	--
Sample N1		2854	2854	n.n.	-14	2868	329	28	2071	127	3.30	609	250	211	7	0.04	2.97
		100	100.0	--	-0.5	100.5	11.5	--	72.5	--	--	--	8.8	7.4	0.3	--	--
Sample N2		10305	10293	12	-67	10360	904	77	7442	560	3.79	556	1102	813	98	0.07	3.31
		100	99.9	0.1	-0.6	100.5	8.8	--	72.2	--	--	--	10.7	7.9	1.0	--	--
Sample N3		12334	12141	193	-170	12310	1028	87	8501	718	3.99	569	1617	1006	159	0.11	3.38
		100	98.4	1.6	-1.4	99.8	8.3	--	68.9	--	--	--	13.1	8.2	1.3	--	--
Sample N4		13215	12891	324	-191	13082	1071	89	9122	721	4.02	569	1900	989	0	0.04	3.36
		100	97.5	2.5	-1.4	99.0	8.1	--	69.0	--	--	--	14.4	7.5	0.0	--	--
Sample N5		14773	14328	445	5	14323	1137	92	9649	764	4.32	565	2231	1305	0	0.03	3.46
		100	97.0	3.0	0.0	97.0	7.7	--	65.3	--	--	--	15.1	8.8	0.0	--	--

Project: 0		Partitioning of Organic Carbon (OC)					Chromatographic Fractionation of Organic Carbon (CDOC)							(UV@254 nm)			
sampl.date	19/6/2008	Approx. Molecular Weights in g/mol: →					>>20.000	~1000 (see separate HS-Diagram)			300-500	<350	<350				
		TOC=DOC+POC DOC=CDOC+HOC Note: POC, hence TOC may be too low					Bio-		Humic			Building	Neutrals	Acids	Inorg.	SUVA	
		TOC	DOC	POC	HOC	CDOC	Polymers	DON	Subst.	DON	Aromaticity	Mol-Weight	Blocks			Colloid.	
		total OC	dissolved	particul.	hydrophob.	hydrophil.	(Norg)	(HS)	(Norg)	(SUVA-HS)	(Mn)				SAC	(SAC/OC)	
		ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	ppb-C	ppb-N	L/(mg*m)	g/mol	ppb-C	ppb-C	ppb-C	(m ⁻¹)	L/(mg*m)
		% TOC	% TOC	% TOC	% TOC	% TOC	% TOC	--	% TOC	--	--	--	% TOC	% TOC	% TOC	--	--
IHE Raw		15905	15716	189	284	15431	1299	103	10299	448	4.33	556	2195	1639	0	0.04	3.64
		100	98.8	1.2	1.8	97.0	8.2	--	64.8	--	--	--	13.8	10.3	0.0	--	--

