Modeling of micro-pollutants removal by a PAC-MF system

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Challenge the future

Modeling of micro-pollutants removal by a PAC-MF system

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Abstract

Nowadays, a large number of organic micro-pollutants are presented in drinking water sources, some methods should be developed to remove them effectively. Activated carbon (AC) adsorption is one of the most cost-effective ways for micro-pollutants removal. In the real situation, the operation of continuously dosed PAC before membrane filtration is widely applied in drinking water treatment while the operation of PAC pre-coated on the membrane is a new approach. This research, therefore, aims at evaluating the micro-pollutants removal efficiency by the pre-coated PAC-MF system. The mechanism of micro-pollutants removal is analyzed. In addition, some Stimela simulations have been done to model the breakthrough line with a limited number of known parameters.

Water from the Schie canal in Delft was coagulated with $FeCl_3$ and then filtered through a PAC-MF system. Atrazine and sulfamethoxazole were chosen as the target micro-pollutants, because of their different hydrophobic/hydrophilic characters. The effluent concentration of the micro-pollutants was monitored every hour during the operational time. In addition, to better analysis the mechanism of micro-pollutants removal, the zeta potential was measured during the whole experiment. To further prove which process is the most important process for the micro-pollutant removal in the system, the micro-pollutants concentration after different step was also measured. After the membrane experiment, some modeling was performed for investigate if it can be applied for practical implications. To obtain the unknown constants K, n, and k_2 value which should be the input to the modeling, a special batch experiment was designed.

The results show that the micro-pollutants removal breakthrough occurred later for smaller PAC particle size than for the larger PAC particle size, and the more hydrophilic micro-pollutant (sulfamethoxazole) broke through faster than the hydrophobic micro-pollutant (atrazine). For a certain micro-pollutant, removed by different sizes of PAC, the k_2 value and the internal area will impact on the PAC breakthrough line. For different micro-pollutants removed by a certain PAC, the hydrophilic/hydrophobic character was the most important influencing factor, and the charge effect also had some influence.

From the modeling part a breakthrough line could be obtained. However the breakthrough line did not match the breakthrough line from the experiment. Only after changing the k_2 value according to the empirical equation, the breakthrough line gave a better match. For the adjustment of the modeling, parameters such as inflow flux, bed height, Freundlich constant K were the most important parameter, influencing the PAC breakthrough line.

Finally it was concluded that the more hydrophilic micro-pollutant (sulfamethoxazole) was not effectively removed by PAC, while for the more hydrophobic micro-pollutant (atrazine), there is not much difference between the large and the small PAC particles during longer filtration times. So the larger PAC is recommended to be applied to remove the hydrophobic micro-pollutants due to the fact of costs.

Key words: activated carbon; adsorption; microfiltration membrane; atrazine; sulfamethoxazole; Stimela

Preface

This thesis is my final thesis for my study at the Faculty of Civil Engineering and Geosciences of the Delft University of Technology. The title of this thesis is: modeling of micro-pollutant removal by a PAC-MF system. For my master thesis, I wanted to do some drinking water experiment, after contact with Lu Jie, they had a topic about micro-pollutants removal by PAC-MF system. After meeting with my supervisor Bas Heijman, we decided that the research would combine with modeling. The experimental research is conducted at Delft University of Technology, laboratory of Sanitary Engineering.

I would like to acknowledge my committee for their huge effort on my project. My professor Luuk Rietveld needs to be thanked for his expertise and critical notes on the research. Also I would like to acknowledge Bas Heijman for the supervision and consultancies, Lu Jie for his advice and supervision during the graduation period.

Also, Arne Verliefde and Arnout D'Haese from Ghent university should be acknowledge for their support on measurement equipment, without the support of nice guide of measurement I cannot get the nice experiment results. Furthermore, thanks for the advice and time from David de Ridder. Finally I would like to acknowledge all people from the laboratory of Sanitary Engineering for their support.

I would like to thank my family and friends for their support and inspiration, especially Cao Yun and Tian Shen. Finally, I would like to thanks my parents for their strongly support on my study, without their support I cannot achieve the result so far.

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Table of Content

List of illustrations

List of tables

1 Introduction

1.1 Problem statement

Clean drinking water is crucial in our daily basic need. The deterioration of drinking water quality will lead to several waterborne diseases such as Cholera, Typhoid, Hepatitis and Diarrhea which result in killing over 3,4 million people each years. Besides the pathogenic micro-organisms remove, the removal of suspend solids, ions and micro-pollutants (such as pesticides, pharmaceuticals or industrial waste products) are also core targets for drinking water treatment, both for health, operational and aesthetic reasons. In this thesis, the focus will be on the removal of organic micro-pollutants.

Traditionally, the safety of drinking water is just focused on microbiological contaminants concentration. However, a survey of US groundwater in 1982 revealed the presence of pesticides and other industrial products(Cotruvo 1985). Nowadays, there is a boarder set of contaminants that are detected in surface waters. Except for pesticides and industrial products which were mentioned in the 1982 survey, the concentration of endocrine disrupting compounds (EDC's), pharmaceuticals, and personal care products such as fragrances, cosmetics and sunscreen are adding to the current drinking water quality. The general term of all those contaminants is organic micro-pollutants, referring to their organic nature and low concentration in surface water. A schematic overview of the pathways that lead to the contamination of drinking water sources by those organic micro-pollutants is shown in Fig.1.

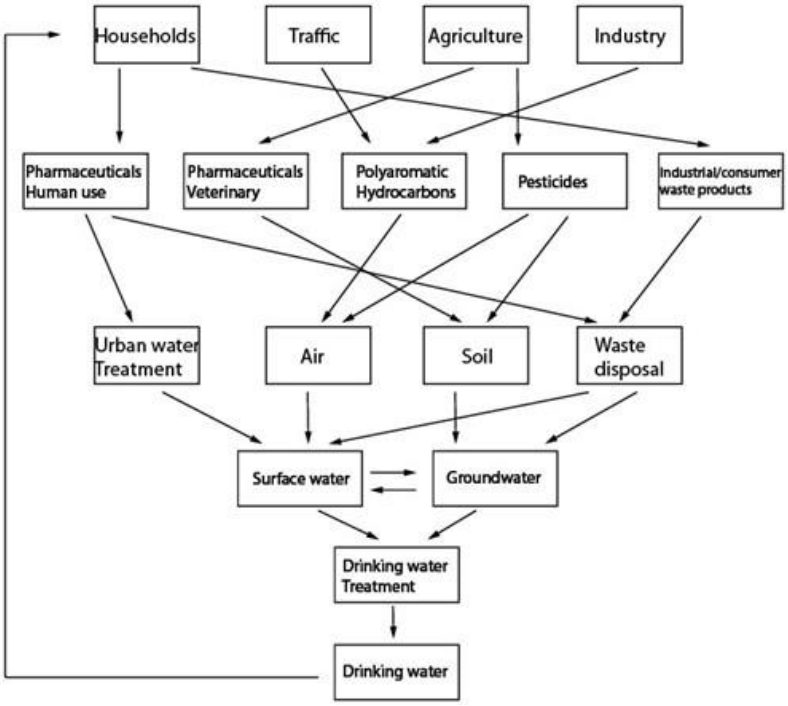

Figure 1: Micro-pollutants pathways (Heberer 2002)

The presence of organic micro-pollutants seriously threatens human health which can be attributed to the interference with hormonal functions such as behavioral development and fertility. Many micro-pollutants accumulate in the environment due to their persistence and increasingly occur in water at measurable

concentrations (Tyler, Jobling et al. 1998; Schwarzenbach, Escher et al. 2006; Gabriel, Routledge et al. 2008). Due to the negative impact on mammals, the regulations and methods for micro-pollutants removal should be given priority(Schäfer, Akanyeti et al. 2011).

Regulation of organic micro-pollutants on the European level is necessary, as rivers and river basins have an international character. In the European Water Framework Directive (WFD; Directive 2000/60/EC), 33 kinds of organic micro-pollutants were chosen as priority hazardous substances (Table 1).

Table 1: European limits for priority (harzardous) pollutants in surface water(de Ridder, Villacorte et al. 2010)

Substance	Concentration(µg/L)	Substance	Concentration(µg/L)
Alachlor	0.3	Hexachlorobutadiene	0.1
Anthracene	0.1	Hexachlorocyclohexane	0.02
Atrazine	0.6	Isoproturon	0.3
Benzene	10	Lead	7.2
Brominated diphenylether	0.0005	Mercury	0.05
		Naphthalene	2.4
Cadmium	0.08	Nickel	20
chloroalkanes	0.4	Nonylphenol	0.3
Chlorfenvinphos	0.1	Oxtylphenol	0.1
Chlorpyrifos	0.03	Pentachlorobenzenes	0.007
1,2-dichloroethane	10	Pentachlorophenol	0.4
Dichloromethane	20	Polyaromatic hydrocarbon	0.05
DEHP	1.3	Simazine	1
Diuron	0.2	Tributyltin	0.0002
Endosulfan	0.005	Trichlorobenzenes	0.4
Fluoranthene	0.1	Trichloromethane	2.5
Hexachlorobenzene	0.01	Trifluralin	0.03

The concentration of micro-pollutants is usually around µg/L or ng/L which is considered too low to directly impact human health, but there is still uncertainty about the long term influence and synergetic effects (mixture toxicity). From an ethical point of view, the presence of organic micro-pollutants, even at low concentrations, is undesirable in drinking water(de Ridder, Villacorte et al. 2010).

1.2 Research Goals and Objectives

The main goal of this research is to investigate atrazine and sulfamethoxazole removal, as model compounds for EDCs, in a hybrid system of powdered activated carbon (PAC) and microfiltration (MF), using relative long filtration times without backwash.

The specific objectives of this study are:

- To investigate the maximum PAC pre-coated capacity on the membrane.
- To investigate the micro-pollutants removal efficiency by PAC-microfiltration system.

- To analysis the breakthrough trend and mechanism of different micro-pollutants by certain PAC.
- To analysis the breakthrough trend and mechanism of certain micro-pollutants by different size of PAC.
- Use modeling (Stimela) to simulate and predict the breakthrough line of PAC with certain input parameters.

1.3 Content of the thesis

In chapter 2, some background information about target micro-pollutant is presented. Furthermore, there is a comparison of the advantages and disadvantages of different methods of micro-pollutants removal. In addition, a review of the mechanisms of micro-pollutants, removed by PAC, is illustrated. Then the performance of the PAC-MF system is described. Lastly, there is an introduction in Stimela modeling and how to determine the calibration parameters, needed as input for Stimela.

In chapter 3, four separation experiments are presented, which include a pre-coating experiment, a membrane experiment, an experiment to determine the removal of micro-pollutants removal in different parts of the system, and a batch experiment. The chapter includes the experimental setup, and the equipment needed for different experiment. In the end, the processes, parameters and the requirements for a modeling environment are defined.

Chapter 4 presents the results of the different experiments. The maximum capacity of the pre-coated PAC was obtained. In addition, the mechanism of micro-pollutants removal by PAC is analyzed and the most influencing factor for PAC breakthrough is discussed. The results of the experiments further prove that the PAC step is the most important step for micro-pollutants removal in the system. The modeling was set up with the results of the batch experiment and a comparison was made of the modeling results and the breakthrough line, obtained by the membrane experiment.

In chapter 5 conclusions are given on the results of the case studies with respect to influencing parameters and mechanisms for micro-pollutants removal by the PAC-membrane system. In addition, some recommendations are given on future application of the PAC-membrane system on micro-pollutants removal in drinking water treatment.

2. Background

2.1 Character of micro-pollutants

2.1.1 Hazard of atrazine

Atrazine (Fig. 2) is one of the herbicides, which was applied in a lot of countries, to control the growth of weed during crop production. Although atrazine is applied to surface soil, it has the tendency to travel with water and normally percolates to groundwater via infiltration. Moreover, because its persistence character in the soil and the slow rate of degradation, atrazine can be detected in groundwater and surface waters all over Europe and North America. When the drinking water was contaminated by atrazine, there is a clear negative impact on birth defects and menstrual problems when the water was

consumed by human. (Papastergiou and Papadopoulou-Mourkidou 2001; Van Maanen, De Vaan et al. 2001; Cerejeira, Viana et al. 2003; Graziano, McGuire et al. 2006) . The European Union legislation banned its use (since 2003) and the use was also restricted in other countries, but it is still detected at levels exceeding the maximum contaminant level imposed for all active substances (U.S. EPA: 3 µg/L; EU: 0.1 µg/L, when expressed as sum of parent compounds and metabolites) (Sass and Colangelo 2006; Belloni, Dessì-Fulgheri et al. 2011).

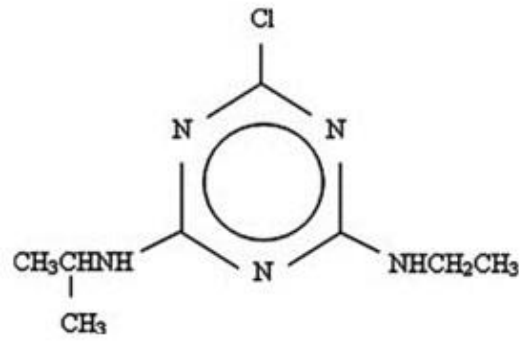

Figure 2: Chemical stucture of atrazine (Hayes, Collins et al. 2002)

The negative impacts of atrazine are various. To be specific, the central nervous system appears to be the primary target site of atrazine influencing the reproductive function(Giusi, Facciolo et al. 2006). It has been shown that atrazine could modulate aromatase activity (Benachour, Moslemi et al. 2007; Fan, Yanase et al. 2007), it increases the level of estradiol circulating in an individual, (Nadzialek, Spanò et al. 2008). The result of vertebrate taxa indicated that atrazine inhibits the development of androgen-mediated ,meanwhile producing estrogen-like effects on individuals(Matsushita, Yamashita et al. 2006). Furthermore, atrazine also leads to feminization in male tadpoles, which could be explained as one of the possible reason for the decreased amount of amphibians in the whole world (Hayes, Collins et al. 2002). Moreover, it has been related with detrimental effects on the immune system activity in rodents(Stoker, Laws et al. 2000). The atrazine not only has negative impacts on animal but also on human beings, it was found that men who are living in intensive agricultural areas have semen of a lower quality , and women who are living there have a higher incidence rate of breast cancer (Swan, Kruse et al. 2003). As a result, agricultural infiltrate, containing atrazine, is one of the most problematic environmental issues(Siripattanakul, Wirojanagud et al. 2009).

2.1.2 Hazard of sulfamethoxazole

Sulfamethoxazole (Fig. 3) is an anti- bacterial sulfonamide. It prevents the formation of dihydrofolic acid, a compound that bacteria must be able to make in order to survive. Although it was once a very useful antibiotic, it is almost obsolete as a single agent today, due to the development of bacterial resistance to its effects. Sulfamethoxazole is now primarily used in combination with trimethoprim, a combination product known as Bactrim or Septra. Sulfamethoxazole was approved by the FDA in 1961. According to the FDA database, all brand and generic formulations of sulfamethoxazole have been discontinued (Prasad 1996).

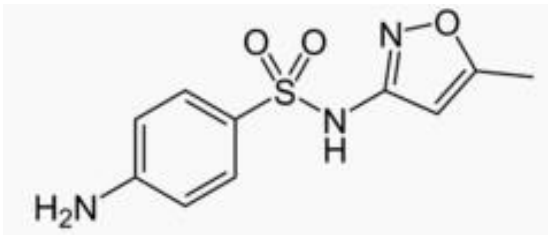

Figure 3: Chemical structure of Sulfamethoxazole (Prasad 1996)

Sulfamethoxazole can produce a variety of side effects that include gastro-intestinal disturbances, hypersensitivity reactions, and a number of haematological abnormalities such as thrombocytopenia, agranulocytosis, megaloblastosis, eosinophilia, and sulfhemoglobinemia. In addition, a significant increase in the percentage of abortions and a decrease in live births have been reported among the later generation of men working in a pharmaceutical factory and exposed to sulfonamides.

Hypotension, pulmonary edema, and elevated serum transaminases have been reported following administration of trimethoprim-sulfamethoxazole to patients with HIV infection. Cholestatic jaundice, thought to be due to hypersensitivity, has been reported with sulfamethoxazole alone.

Neurologic side effects are uncommon and include headache, depression, and hallucinations. A single case of acute psychosis has been associated with the routine use of oral trimethoprim-sulfamethoxazole (TMP-SMX). This reaction is believed to be due to the SMX component of the drug.

Hematologic side effects are unusual and include thrombocytopenia, leukopenia, agranulocytosis, and hemolytic, megaloblastic, and aplastic anemias. Methemoglobinemia induced by sulfamethoxazole has been reported. There is in vitro evidence for a sulfamethoxazole-associated antiplatelet antibody. Serologic studies (flow cytometry) on a man with profound and symptomatic thrombocytopenia, associated with trimethoprim-sulfamethoxazole (TMP-SMX), revealed significant SMX-dependent platelet-reactive antibody. These findings are consistent with a diagnosis of SMX-induced immune thrombocytopenia.

Renal side effects occur occasionally, probably due to sulfa crystalluria. Sulfamethoxazole may induce sulfa crystal precipitation in renal tubules. Frequent monitoring of serum creatinine and urinalysis is recommended during sulfamethoxazole therapy in patients with renal insufficiency.

Cholestatic hepatitis associated with sulfamethoxazole therapy may present with other signs of hypersensitivity, such as rash, fever, and eosinophilia. Hepatic side effects are rare but can be serious. Isolated cases of jaundice due to cholestasis have been reported. Fulminant hepatic failure has occurred in a few patients treated with trimethoprim-sulfamethoxazole and is likely due to the sulfamethoxazole component.

Sulfamethoxazole, like other sulfonamides, may induce hypoglycemia by stimulating pancreatic islet cells to secrete insulin. A single case of hypoglycemic stupor associated with trimethoprim-sulfamethoxazole has been reported.

2.2 Methods for micro-pollutant removal

In order to guarantee the safety of drinking water at the tap, the World Health Organization (WHO) and the U.S. Environmental Protection Agency (E.P.A.) have issued guidelines for humanly safe drinking water which contain the target concentrations for several contaminants. Furthermore, the development of methods of micro-pollutants removal is necessary (Verliefde, Cornelissen et al. 2007). In consequence, advanced treatment technologies are required to effectively eliminate such micro-pollutants.

2.2.1 NF/RO

Membrane filtration is a major advanced technology in drinking water treatment which can control the effluent water with a good quality. For micro-pollutants removal, nano-filtration (NF) and reverse osmosis (RO) are the most suitable solutions (Rogers 1996; Van der Bruggen, Schaep et al. 1999; Kiso, Kon et al. 2001; Nghiem and Schäfer 2002; Kimura, Amy et al. 2003; Kimura, Amy et al. 2003; Kimura, Toshima et al. 2004; Jones, Voulvoulis et al. 2005; Kim, Amy et al. 2005; Agenson and Urase 2007; Lin, Chiang et al. 2007; Libotean, Giralt et al. 2008; Ozaki, Ikejima et al. 2008).

The mechanism of membrane technologies removing micro-pollutants is according to their pore size. The range of molecular sizes of micro-pollutants is 0.6nm-1.6nm. The pore size for a nano-filtration membrane is 0.001-0.01µm and for a reverse osmosis membrane is smaller than 0.001µm (Fig.4). As a result, nano-filtration and RO can remove micro-pollutant effectively.

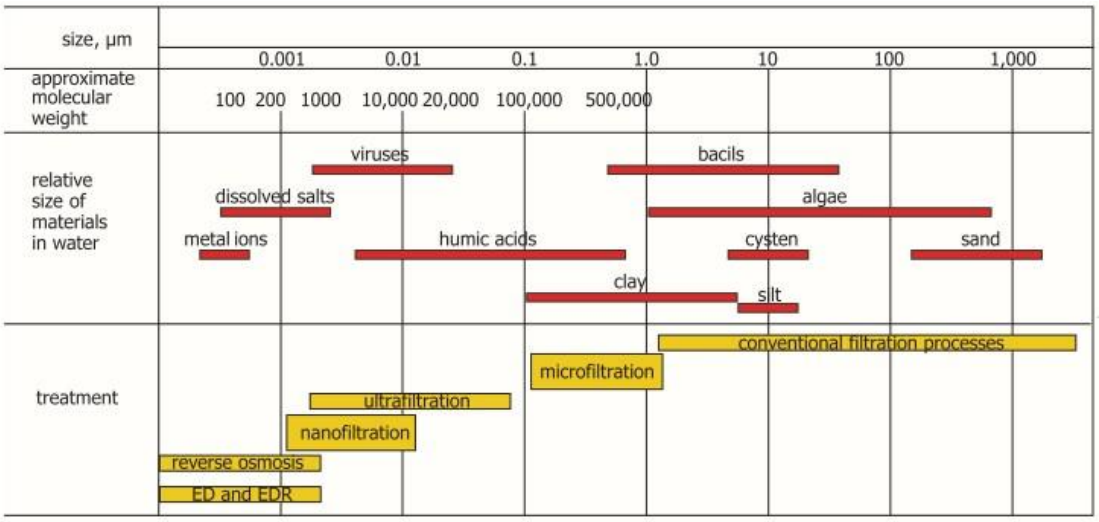

Figure 4: Overview of different filtration processes and sizes of compounds removed (van Dijk, Verberk et al. 2009)

The main advantage of micro-pollutants removal by NF/RO is that the removal efficiency is the highest among all the advanced treatment technologies. However, there are still some drawbacks of membrane technology to remove micro-pollutants. For instance, the membranes must be managed under high pressures, which lead to higher operational costs.

2.2.2 Activated carbon

Activated carbon is widely used in drinking water treatment for the removal of organic micro-pollutants because of its porous structure and large internal surface area (Pelekani and Snoeyink 1999; Quinlivan, Li

et al. 2005). An overview of different technologies which are used for drinking water treatment in Netherlands is shown in Table 2. The table illustrates that almost every company has chosen activated carbons for micro-pollutants removal.

Table 2: Overview treatment technologies used by Dutch water companies that treat surface water (Pelekani and Snoeyink 1999)

Water company	Location	Intake reservoir	infiltration	Aeration	Coagulation/flocculation	Rapid sand filtration	Softening	Ozone	***Activated Carbon***	Advanced oxidation	Membrane filtration	UV disinfection	Chlorination	Slow sand filtration
WML	Heel	√	√	√		√			√			√		
	Roosteren		√	√		√						√		
Evides	Kralingen	√			√	√	√	√	√				√	
	Berenplaat	√			√	√	√		√			√	√	
	Ouddorp		√	√	√	√			√		√			
	Baanhoek	√		√	√	√	√	√	√				√	
Dunea	Katwijk		√	√	√	√	√		√					√
	Scheveningen		√	√	√	√	√		√					√
	Monster		√	√	√	√	√		√					√
Vitens	Weerseloseweg		√		√			√	√			√		√
PWN	Andijk	√			√	√			√	√			√	
	Bergen	√	√	√	√	√			√					
	Mensink	√	√	√	√	√	√		√				√	
	Heemskerk	√			√	√			√		√			
Waternet	Leiduin		√		√	√	√	√	√					√
	Weesperkarspel	√			√	√	√	√	√			√		√
Waterbeddrijf Groningen	Depunt	√		√	√	√			√			√		√

Adsorbent pore size distribution (PSD) is one of the most important characters which impact the activated carbon adsorption capacity. PSD gives the information about the total pore volume that can be used during the adsorption process. Normally, the pore size is divided into four groups according to the classification of the International Union of Pure and Applied Chemistry (IUPAC): macro-pores (>500 Å), meso-pores (20–500 Å), secondary micro-pores (8–20 Å) and primary micro-pores (<8 Å)(Fig.5) (Lastoskie, Gubbins et al. 1993)

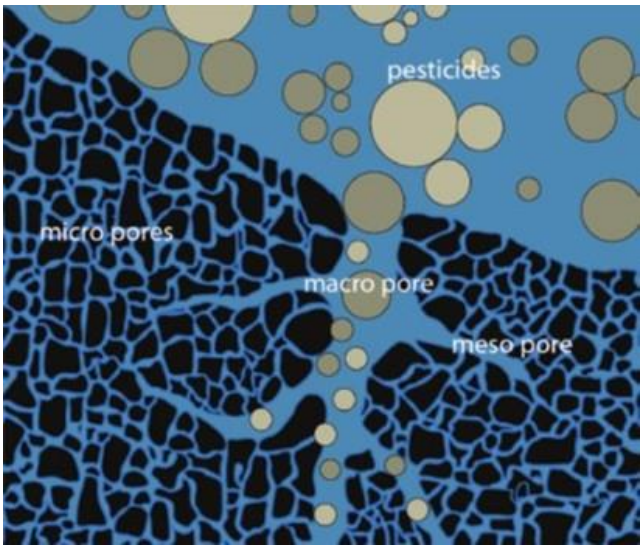

Figure 5: Pore types in activated carbon (van Dijk, Verberk et al. 2009)

Using different molecular dyes as target contaminant, (Kasaoka, Sakata et al. 1989) found that adsorbates with a size similar to the pore size of the carbon adsorbe better because of the greater number of contact points between the molecule and the adsorbent. Although macro- and meso-pores are important to provide quick transport of the solutes to the micro-pores, micro-pores make up the most internal surface area (90%) of activated carbon and the majority of the adsorption occurs within them (Pelekani and Snoeyink 1999). For instance, (Ebie, Li et al. 1995) did an experiment about activated carbon removing single halogenated organic compounds, the result indicated that most of the compound was adsorbed within pore sizes less then15 Å.

The affinity of a solution for the activated carbon surface is dependent on different factors, for example, the presence of specific functional groups and the surface charge of the carbon. Those factors are ambiguous and not constant, solutes may bind with the specific functional groups on the carbon, but water molecules can also do this, decreasing the adsorption surface available for the solutes. The surface charge of the carbon is pH dependent, and will also change when solutes adsorb onto the surface.

Except the capacity of micro-pollutants removal, another advantage of activated carbon is that the investment and operational costs is lower than other kinds of advanced technologies.

However, there are also some drawbacks of activated carbon. One of them is the competition with natural organic matter (NOM). If the raw water contains NOM, the NOM will also be adsorbed by the activated carbon, which creates a competitive relationship with micro-pollutants. Some researches indicated that the NOM adsorption precedes the adsorption of micro-pollutants (Summers, Haist et al. 1989; Speth 1991; Carter and Weber Jr 1994; Kilduff, Karanfil et al. 1998; Knappe, Snoeyink et al. 1999), while others concluded that those two processes occur in same time(Najm, Snoeyink et al. 1991; Newcombe, Drikas et al. 1997; Gillogly, Snoeyink et al. 1998; Knappe, Matsui et al. 1998; Newcombe, Morrison et al. 2002). However, both situations lead to competition of NOM with micro-pollutants, which, as a result, decreases the removal efficiency of the micro-pollutants. On top of that, another drawback of

activated carbon is that, after certain filtration time, the activated carbon will breakthrough, and has to be regenerated.

2.2.3 Advanced oxidation

Ozonation (O_3) is an effective way to remove different kinds of environmental pollutants such as dyes, herbicides and other pesticides in an aqueous solution (Lambert, Graham et al. 1993; Chu and Ma 2000). Ozone (O_3) is widely used in micro-pollutants removal because of its oxidation capacities. The mechanism of ozone removing organic micro-pollutants is that micro-pollutants can directly react with O_3 or with hydroxyl radicals ($OH^{\cdot}$), resulting from ozone decay in water(von Gunten 2003). O_3 reacts selectively with organic compounds and second order rate constants vary over 10 orders of magnitude, whereas $OH^{\cdot}$ is a less selective oxidant and its reaction with the majority of the organic compounds is nearly diffusion controlled (von Gunten 2003). Usually ozone is not applied alone, but is combined with H_2O_2, a so-called advanced oxidation process (AOP). AOPs are based on the enhanced formation of $OH^{\cdot}$., which can reduce the reaction time required for micro-pollutant transformation (Acero and Von Gunten 2001). In addition to ozone, ultraviolet radiation (UV) combined with H_2O_2 can also react with micro-pollutants. The combination of UV with H_2O_2 can also lead to micro-pollutant transformation by direct photolysis and by reactions with $OH^{\cdot}$, formed during the process (Katsoyiannis, Canonica et al. 2011).

However, those processes produce an array of unknown by-products with an often equal or higher toxicity. For example, ozone itself does not form halogenated DBPs, however, if bromide is present in raw water bromate may be formed. Other ozonation byproducts include organic acids and aldehydes.

After the above analyses, it can be concluded that, although most of those advanced technologies have a high efficiency for micro-pollutants removal, several drawbacks may occur. Therefore, in the following the focus will be laid on the removal of micro-pollutants by activated carbon.

2.3 Mechanisms of micro-pollutants removal by activated carbon

2.3.1 Certain micro-pollutant removal by different activated carbons

There are several factors that can influence the micro-pollutants removal efficiency by activated carbon such as pore size, charge effect and the hydrophobic/hydrophilic characters of the activated carbon.

Pore size

Compared to the external adsorption area, the internal surface area is the most dominant for the total available adsorption capacity(Li, Quinlivan et al. 2002). This can be explained by:

1) Stronger Van der Waals interaction as the distance between the solute molecule and the carbon surface is shorter.

2) Size exclusion may occur at the pore entrance. As larger molecules are retained, there is less competition for adsorption sites for the smaller molecules.

However, the large molecules can also block the micro-pores. For the removal of micro-pollutants, the optimal pore size is 1.3-2 times the target molecule size (Li, Quinlivan et al. 2002; Quinlivan, Li et al. 2005).

Charge

The charge of the activated carbon is dependent on pH. Functional groups with an acid character, such as phenol (-OH) and carboxyl (-COOH), may dissociate at higher pH, releasing their protons (H^+) and obtaining a negative charge. A positive surface charge can be attributed to basic functional groups, such as amines(-NH_2), chromenes and pyrenes (both O-containing), as these functional groups protonate at lower pH taking up H^+ and obtaining a positive charge (Moreno-Castilla 2004).

Hydrophobicity

Activated carbon has high quantities of O-containing or N-containing functional groups and has a high affinity for water, and are thus considered to be hydrophilic(Li, Quinlivan et al. 2002; Quinlivan, Li et al. 2005). As hydrophilic carbon promotes the bonding with water, the number of available adsorption sites for micro-pollutants is reduced. Also water clusters can be formed, which can block the entrance of the micro-pores (Franz, Arafat et al. 2000; Villacañas, Pereira et al. 2006). It was found that the more hydrophilic the activated carbon is, the less micro-pollutants were adsorbed, even when the solute was able to form hydrogen bonds with the functional groups (Franz, Arafat et al. 2000).

2.3.2 Different micro-pollutants removal by same activated carbon

According to literature(de Ridder, Villacorte et al. 2010), there are three factors influencing the removal efficiency for different micro-pollutants removed by same activated carbon, which are the molecular size (molecule weight), charge and hydrophobic/hydrophilic character of the micro-pollutants. Details of how those factors influence breakthrough will be presented in section 3.2.2.

2.4 PAC-MF system

Usually powdered activated carbon (PAC) is applied as an individual step in drinking water treatment. However, several researches indicated that, if PAC is used in combination with low pressure membranes, PAC can not only remove contaminants (e.g. natural organic matter (NOM), synthetic organic chemicals (SOCs) and micro-pollutants) (Adham, Snoeyink et al. 1991; Pirbazari, Badriyha et al. 1992; Adham, Snoeyink et al. 1993; Chang and Benjamin 1996; Chang, Choo et al. 1998), but also control membrane fouling. In this case, the pre-coated PAC-MF system is investigated to test the micro-pollutants removal by different PAC.

The advantage of the PAC-MF system is that the suspended PAC suspended can adsorb low molecular organic compounds that cannot be removed by the membranes alone. The membranes provide a physical barrier preventing the passage of the PAC, thus ensuring the retention of the organic compounds adsorbed on the PAC(Mozia, Tomaszewska et al. 2005).

The PAC-MF system can be operated in three different modes: PAC pretreatment; PAC adsorption occurring simultaneous with membrane filtration; and pre-coated PAC on the membrane. The performance will be discussed in relation to fouling control and contaminant removal aspects.

2.4.1 PAC as a pre-treatment process

In the majority of the PAC-MF systems, the PAC is a pretreatment process. Some researchers found that it positively impact on membrane fouling. (Khan, Takizawa et al. 2011) indicated that the presence of

PAC reduced the molecules that enhance membrane fouling. In addition, compared to the situation without PAC dosage, the presence of PAC not only increases the flux when treating source water containing humic acid, but also increases the flux recovery after backwashing. (Li, Zhang et al. 2011) illustrated that the flux recovery following the physical backwashing was around 80% for a ultrafiltration process alone, but the recovery was over 90% with the addition of PAC.

In addition, (Xia, Liu et al. 2007)) found that PAC addition to the PAC-MF system enhanced organic matter removal. The combined process of PAC/UF reached to 41% removal of COD_{Mn}, 46% removal of DOC and 57% decrease in UV254 absorbance.

2.4.2 PAC adsorption simultaneous with membrane filtration

There is some literature that proves that PAC has a positive influence on membrane fouling. (Zhang, Tian et al. 2011) indicated that the addition of PAC to an immersed UF reactor significantly alleviated the development of trans-membrane pressure. In addition, Gai compared the without (System A) to the with dosage of PAC system (20 g/L (System B)). During an experimental period of 65 days, the value of TMP (trans-membrane pressure) in System B increased by 16 kPa, while the value of TMP in System A increased to 61 kPa after 48 days. As a result, the continuous filtration time was extended by using PAC(Gai and Kim 2008)

For the removal of micro-pollutants, previous research has shown that the PAC-MF can remove micro-pollutants effectively. It was indicated that the PAC in PAC-MF system can effectively remove 17β-estradiol(Lee, Lee et al. 2009) and atrazine(Li, Snoeyink et al. 2003). It was also found that the addition of PAC enhanced the removal of dissolved organic carbon, UV_{254}, and microcystins (Zhang, Tian et al. 2011).

2.4.3 Pre-coat membranes with PAC

There is a special situation for the PAC-MF system where the PAC is pre-coated on the membrane surface. The difference with the previous two situations is that the retention time in this case is rather short, and normally operation is without backwash. The thickness of the PAC layer is a key factor which influences the performance of the PAC-MF system.

Some of the main advantages of the PAC pre-coated membrane operation are:

- Simple and single step operation without any pretreatment for secondary and tertiary treatment,
- Avoids large addition of PAC into the influent tank, which reduces the strain on the membrane,
- Significantly lowers membrane fouling, which could improve membrane life, enhance process performance and reduce membrane cleaning time.

(Thiruvenkatachari, Shim et al. 2006) indicated that by pre-coating the membrane surface with PAC, the membrane fouling was effectively minimized, as the rates of decline of permeate flux was significantly reduced. The type of PAC coated on the membrane and the amount coated could be the key factors in deciding the performance of the system. Further, when using the pre-coated membrane, addition of small amounts of PAC in the tank enhanced organic removal efficiency and maintained the permeate flux.

Moreover, it was also proven that the suitable thickness of the PAC layer could prevent pollutants from diffusing to the exterior and interior of the support layer of the membrane, thereby alleviating membrane fouling(Ye, Zhang et al. 2006).

2.4.4 Fractions range removed by PAC

To clearly understand the mechanisms of the PAC effect on membrane fouling, researchers focus on the molecule size of NOM that is removed by PAC and try to determine if those molecules have influence on membrane fouling. However, the results are controversial. Different researchers had different conclusions about the range of NOM molecular size. Howe and Clark (2002) indicated that particulate matter (larger than 0.45μm) was relatively unimportant in fouling as compared to dissolved matter. Very small colloids, ranging from about 3-20 nm in diameter, appeared to be important membrane foulants. After that, Howe and Marwah illustrated that the component of natural organic matter (NOM) smaller than 100 kDa contributes relatively little to fouling during filtration of either raw or coagulated water. The fraction between 1μm and 100 kDa contributed significantly to fouling(Howe, Marwah et al. 2006). Furthermore, Lin found that for the humic substances, the PAC was ineffective in removing those apparent molecular weight(AMW) fractions less than 300 or greater than 17 000 Da, the higher the PAC dosage, the more removal in the middle range of the AMW factions(Lin, Huang et al. 1999). However, in the result of Lee, the particles of the size range of 0.2–1.2mm caused a significant impact on membrane fouling in all cases with or without coagulation(Lee, Bae et al. 2007). Moreover, in Kim's research, he suggested that organic matter in the molecular weight ranges 300–2000 and 20,000–40,000 Da were mainly responsible for fouling(Kim, Hong et al. 2006)

2.5 Coagulation effect on membrane fouling

Because of the membrane fouling, PAC could not stay for a long time on the membrane. Therefore, some solutions should be made to avoid membrane fouling, and keep PAC staying on membrane for longer periods. Many studies indicated that adding a coagulation step is one of the solutions. Some experiments presented that with coagulation pre-treatment, the flux decline was substantially improved (Choi, Kim et al. 2008). Lee found that the combined coagulation–UF membrane process can remove colloids, which lead to membrane fouling, and also improve the removal of dissolved organic matter (DOM) (Lee, Bae et al. 2007). The more coagulant dose is performed the better the permeate flux. By treating the surface water which contains humic acids (HA), Xu found that for the dosage of Al in low concentrations (1mg/L), the flux at the end of the filtration time is 40% of initial flux. However the value increased to 75% if the coagulant dosage is 5mg/L(Xu, Gao et al. 2011). Furthermore, Zheng showed that the ratio of permeate flux and influent flux decrease followed the decrease in $AlCl_3$ dosage, and the lowest ratio occurred at no coagulant dosing(Zheng, Plume et al. 2012). The presence of coagulation decreases the TMP when filtrating tap water, the TMP value for the membrane without coagulant is twice as high as the TMP value in the coagulation-membrane system(Yu, Liu et al. 2013).

Several studies also represented the situation when coagulation was put before the PAC-MF system. The membrane fouling can then be well controlled. It was demonstrated that treatment by coagulation combined with the PAC-MF system successfully prevented short-term fouling of MF, whereas the

treatment without PAC could remove most of the DOC but did not remove the colloidal components, being unable to prevent fouling(Fabris, Lee et al. 2007). Furthermore, Shon indicated that the effect of PAC and coagulation on membrane fouling alone is rather limited and they compared the results with effect of the combined system (coagulation-PAC-MF) on membrane fouling. They concluded that the combined system is much better(Shon, Vigneswaran et al. 2004).On top of that the advantage of the coagulation-PAC-MF system is not only the control of membrane fouling, but also, the final effluent water quality is improved. Haberkamp found that a combination of coagulation and adsorption yields the superposition of the individual elimination rates in terms of biopolymer removal (Haberkamp, Ruhl et al. 2007). From the results of Guo it can be concluded that pretreatment by coagulation and adsorption led to almost complete phosphorus and organic removal while reducing the membrane clogging. This pre-flocculation improved the dissolved organic removal only marginally (from 20% to 40%) whilst the pretreatment of adsorption increased the organic removal to more than 98%. The decline in filtration (permeate) flux of microfiltration was reduced by the incorporation of these pretreatment methods(Guo, Vigneswaran et al. 2004).They also did a further experiment to illustrate that the coagulation/flocculation and adsorption pretreatment is the best for membrane fouling management: (1) flocculation alone as a pretreatment could effectively remove the large molecular weight organic matter from 30,000 to 60,000 Daltons; (2) flocculation, together with adsorption as a pretreatment to MF, could remove both large and small molecular weight organics; (3) flocculation as a pretreatment was significantly better than adsorption in improving the critical flux; (4) critical flux increased when flocculation-adsorption was applied(Guo, Vigneswaran et al. 2005).

2.6 Modeling

2.6.1 Stimela

Usually batch and column experiments are carried out to assess the efficiency of activated carbon to remove micro-pollutants, but considering the large amount and the different kind of micro-pollutants in current and future drinking water sources, a modeling method to predict the water quality is necessary and cost-effective. However, this does not replace the experimental work, but it gives a fast estimation about which kind of micro-pollutants can be (poorly) removed by certain activated carbons.

Stimela modeling was developed to model the effluent water quality after different water treatment steps(Worm, van der Helm et al. 2010). The Stimela modeling was developed in Matlab/Simulink^{tm}. Partial differential equations are numerically integrated and variation of water quality parameters in time and space can be estimated. The individual treatment steps can be connected to each other forming a complete drinking water treatment system. As a result, the effect of operational changes in preceding treatment processes can be evaluated (Rietveld 2005).

Some modeling with Stimela was done for drinking water quality prediction, such as for softening(van Schagen, Rietveld et al. 2008) and ion exchange(Cornelissen, Moreau et al. 2008). For adsorption, Stimela can be used to model the breakthrough during PAC/GAC filtration.

In this case, Stimela is used for simulating the breakthrough of a with PAC pre-coated layer on a membrane. However, Stimela was designed for modeling a column of granular activated carbon and in this case the PAC is just thin layer on the membrane. Nevertheless, the PAC layer can also be considered a filter and treated as a filtration column.

2.6.2 Simulation of adsorption mechanism in Stimela

Adsorption is a dynamic process, where adsorbates are continually adsorbed onto and desorbed from the adsorbent. When the amount of adsorbed equals the amount of desorbed, the system is in equilibrium which is dependent on the concentration in the water and the temperature.

In adsorption modeling, the distribution of the adsorbate between the two phases (the bulk solution and the adsorbent) is often described in terms of isotherms. The amount of solute adsorbed per unit of adsorbent (q) as a function of the equilibrium concentration of the solute in the bulk solution (C_e), at a constant temperature is called adsorption isotherm (Schippers et al., 2007a).

$$q = f(C_e) \tag{1}$$

In STIMELA the Freundlich isotherm was used to describe equilibrium, under a certain temperature (Equ.2). The Freundich model assumes heterogeneity of adsorption sites, and is considered as an empirical model which can only be used at lower and intermediate solute concentrations, as the model does not include a maximum adsorption capacity(Pikaar, Koelmans et al. 2006).

$$q_e = K{c_e}^n = \frac{X_e}{m} \tag{2}$$

Where:
q_e = equilibrium loading (mg/kg);
K = Freundlich constant $((g/kg)(g/m^3)^{1/n})$;
c_e = equilibrium concentration (g/m^3);
n = Freundlich constant;
Xe = equilibrium mass of adsorbed adsorbate (g);
m = mass of adsorbent (g).

The adsorption of an adsorbate onto the surface of an adsorbent involves a number of steps that occur in series as mentioned below:

- Bulk solution transport – migration of bulk solution
- External (film) transport – external mass transfer
- Internal (pore) transport – internal mass transfer
- Adsorption – formation of adsorption bond between the adsorbate and adsorbent

The transport steps occur in series, so the slowest step, called the rate determining step, will control the rate of removal. For modeling we mainly consider the last three steps external mass transfer, internal mass transfer and adsorption because Bulk transport is so fast and it cannot be the rate determining step

(S.Sharma, 2007).

To better understand the breakthrough principle, a packed bed column of GAC/PAC can be divided into several layers. At startup (t = 0), the carbon is fresh in the entire packed bed, i.e. it has an actual loading of 0 (q_e = 0). Following Freundlich, the actual c_e at the surface of the activated carbon grain is then also 0 and the difference (c_1-$c_{e,1}$) is highest. One layer lower in the bed, the carbon is still not loaded (q = 0), but the initial concentration in this layer is lower because adsorption took place in the layer above. The difference (c_2-$c_{e,2}$) is lower, and consequently adsorption rate will be lower in this layer. This line of thought can be extended for the other layers. This is also illustrated in Fig. 6;

Then, one time unit later (t = Δt). In the top layer, adsorption took place. This changes the actual q in this layer to a new value (depending on how much of the compound is adsorbed), and with the Freundlich equation, the actual c_e at the surface of the activated carbon grain can be calculated. This will be higher than 0, so the difference (c_1-$c_{e,1}$) in the top layer is lower at t = Δt than it was at t=0, and the adsorption rate will be lower. Because of that, c_2 will be higher in the next layer, and depending on the amount of the adsorbed compound in this next layer, (c_2-$c_{e,2}$) can either be higher or lower. This effect is illustrated in Fig. 7.

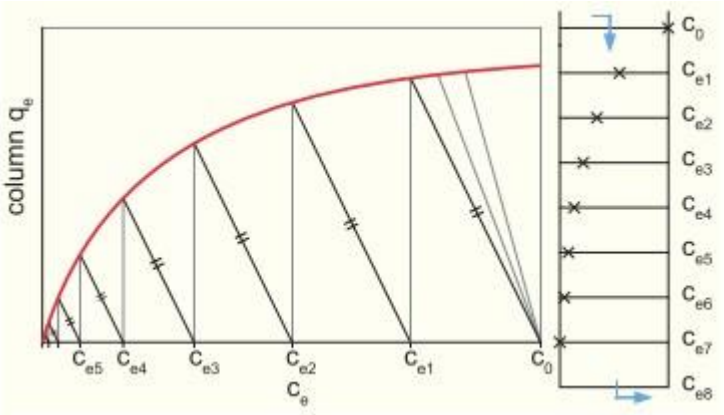

Figure 6: Determining effective carbon loading using the adsorption isotherm - batches in series (van Dijk, Verberk et al. 2009)

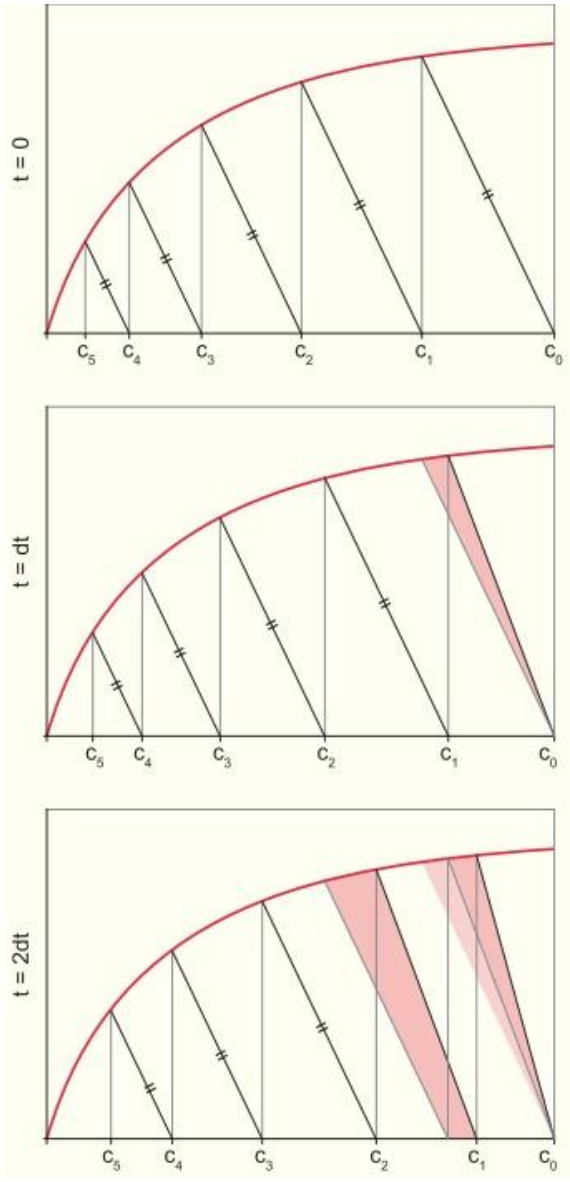

Figure 7: Effect of carbon loading (van Dijk, Verberk et al. 2009)

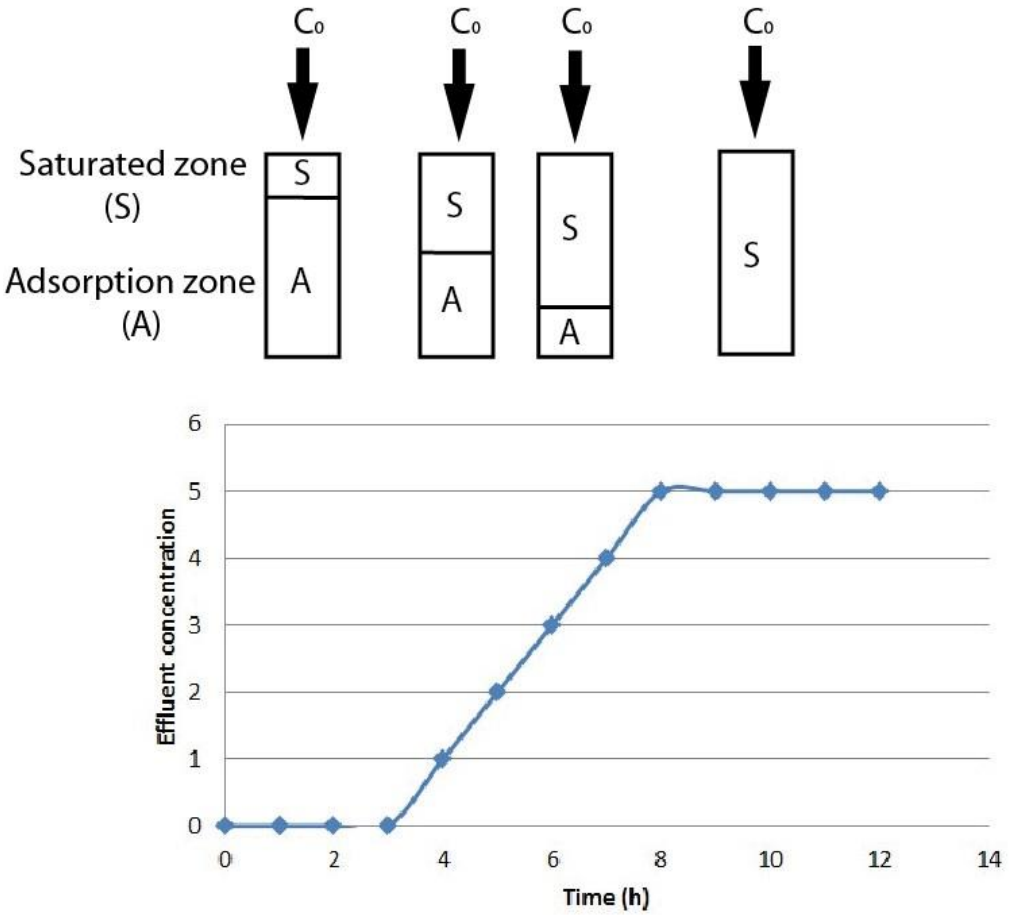

Figure 8: Breakthrough in a packed bed adsorption column

2.6.3 Constant determination

For the Stimela model, the Freundlich constants (K, n) and the kinetic constant (k_2) are crucial inputs. Those constants are depending on the character of the PAC and target micro-pollutants. The way those constants are determined is presented below.

Freundlich constants (K, n)

When Equ. 2 is expressed in logarithmic terms, the empirical equation becomes:

$$\log q_e = \log K_F + n_F * \log C_e \quad (3)$$

When the equilibrium concentration of micro-pollutants is measured, and the initial concentration of micro-pollutants and the mass of the adsorbent are known data, a linear adsorption isotherm can be obtained. The slope of the line is the 'n' value and Y-axis intercept is ln(K) value(Fig. 9).

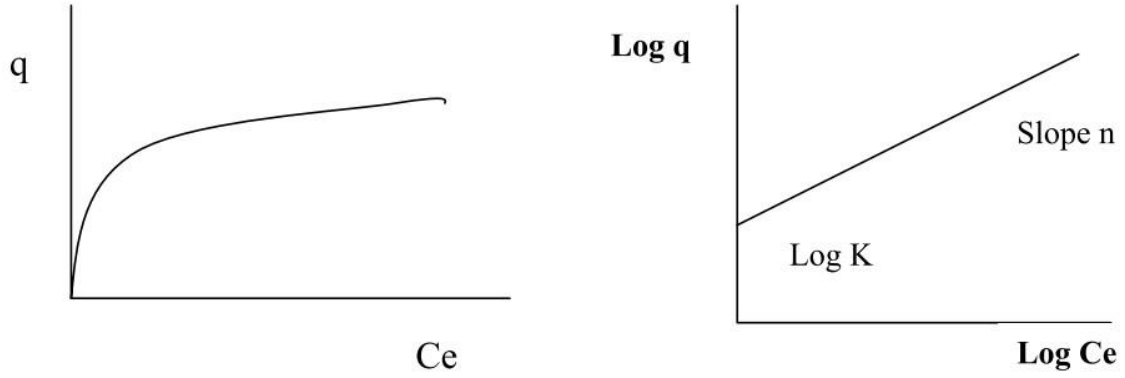

Figure 9: Freundlich Isotherm

Kinetic constant (k_2)

The derivation of the kinetic constant (k_2) is according to the equation below:

$$C_t = (C_0 - C_{eq})e^{-k_2 t} + C_{eq} \quad (4)$$

Where:

C_t = concentration at different time intervals (µg/L);

C_o = the initial concentration at time t=0 (µg/L);

C_{eq} = equilibrium concentration (µg/L);

t = operational time (h).

In Equ. 4 the initial concentration of micro-pollutants and the operational time are known , while the equilibrium concentration and the concentration in time can be measured. The unknown value is the k_2 value that can be calibrated.

Transport through a PAC/GAC solumn

For the transport through the PAC/GAC column the overall advection-dispersion equation is used:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - \frac{u}{\varepsilon}\frac{\partial c}{\partial x} - \frac{\rho}{\varepsilon}\frac{\partial q}{\partial t} \quad (5)$$

Where:

c = influence concentration (g/m^3)

t = reaction time (s)

D_x = dispersion coefficient

x = distance in the packed bed (m)

u = surface loading of filter (m/s)

ε = porosity

ρ = bulk density of carbon (kg/m^3)

q = loading of carbon grain (g/kg)

In the above equation the accumulation of the adsorbed amount ($\frac{\partial q}{\partial t}$) of the measured species is a function of the difference between the actual adsorbed amount (q_t) and the adsorbed amount (q_{ev}) in equilibrium and a kinetic rate constant k_2. In this so called Linear Driving Force equation(LDF) (Equ. 5), k_2

is the overall kinetic rate constant covering film diffusion as well as pore diffusion(Heijman, van Paassen et al. 1999).

$$\frac{\partial q}{\partial t} = k_2(q_{ev} - q_t) \quad (6)$$

The kinetic constant k_2 is mainly depending on the pollutant diffusion rate and the size of the adsorbent.

On top of that, Rietveld and de Vet (2009) also demonstrated that the differential equation for internal mass transport can be written as function of diameter of the carbon grain.

$$\frac{\partial q}{\partial t} = \frac{6}{d_p}\beta(Kc^n - q) \quad (7)$$

Where
d_p= diameter of carbon grain (m)
β = transfer coefficient

Substituting equation 2 into equation 6, and comparing with equation 7, the relationship between PAC diameter and k_2 can be obtained (Equ 8).

$$k_2 = \frac{6}{d_p}\beta \quad (8)$$

Where
d_p= diameter of carbon grain (m)
β = transfer coefficient

According to equation 8, the PAC diameter and the k_2 are inversely proportional: the larger the PAC particle size is smaller the k_2 value.

3 Material and method

3.1 Pre-coating experiment

The purpose of the pre-coating experiment was to investigate the maximum PAC pre-coating capacity on the membrane. Two sizes of commercial (Norit) PAC were used; the nominal diameter of Super SA is 5µm and of super SA G is 21µm (Table 3). The PACs were prepared by rinsing in demi water for 24 hours before the experiment, which aimed to remove the air bubbles from the pores of the PAC. Different amounts of PAC(1g, 3g, 5g, 6.5g, 8g and 10g) were dosed to a mixing tank (5L), so the PAC dosages in the different experimental scenarios was 0.2g/L, 0.6g/L, 1 g/L, 1.3g/L, 1.8g/L and 2g/L respectively. Then the powdered activated carbon solution was filtrated with ceramic membranes (right in Fig. 10)(parameters are shown in Table 4) for different times (5 minutes, 10 minutes and 15 minutes) with a flux of 180 L/(m^2*h). During this step demi water was filtrated to prevent initial membrane fouling. In order to prevent PAC settling, a stirrer was used. After the pre-coating experiment the membrane was totally black as shown in Fig 10 (left).

Table 3: Parameter of PAC

Description	Parameter	
	SA SUPER	SA SUPER G
Total surface area	1150 m^2/g	1100 m^2/g
Pore diameter	5 µm	21 µm
Apparent density	250 kg/m^3	370 kg/m^3

Table 4: Parameter of membrane

Description	Parameter
Membrane surface area	0.11m^2
Nominal pore size	0.1µm
Membrane type	Dead end mode

Figure 10: Blank membrane (right) and pre-coating membrane (left)

After filtration, the liquid remaining in the tank was collected. After removing the water from the tank and weighing the mass of the PAC, the PAC left on membrane can be obtained by determining the difference of the prepared solution and the remainder in the tank.

3.2 Membrane experiment

3.2.1 Experiment setup

Canal water (Schie canal, Delft, The Netherlands) was used as the feed water in this research. Feed water qualities are presented in Table 5. To make the same water quality in each experiment, 1000L canal water was taken and stored during 30 minutes before each experiment. Membrane filtration was operated a constant flux of 60L/m^2 h, using the same membrane and PAC as in the pre-coating experiment. In-line coagulation/flocculation was also adopted in this research. The flocs from the flocculation process were not removed by sedimentation before membrane filtration. The in-line coagulation was composed of a coagulant/pre-coated PAC injection point, a static mixing part, tubing for fast mixing and tubing for slow mixing (flocculation) (Fig.11 and Table 6). $FeCl_3 \cdot 6H_2O$ was used as coagulant using 8mg/l Fe^{3+} concentration. During the experiment, water flowed through the membrane that was pre-coated with PAC particles and the filtration time was12 hours. A flocs cake and a PAC layer were formed during the filtration process. 2µg/L Atrazine and sulfamethoxazole was used as the target micro-pollutants within this test. To perform good mixing with the feed water, the micro-pollutants were dosed before the static mixing part.

Table 5: Water quality of the Schie Canal water

Parameter	Average Value
pH	7.7
Temperature	12.3 °C
Turbidity	2.34NTU

DOC	16.49mg/l
UV254	0.320cm^{-1}
Conductivity	888μs/cm

Table 6: Static mixer, coagulation and flocculation parameter

	G-value	Contact time
Static mixer	1088 s^{-1}	0.4s
Coagulation	386 s^{-1}	56s
Flocculation	19 s^{-1}	1500s

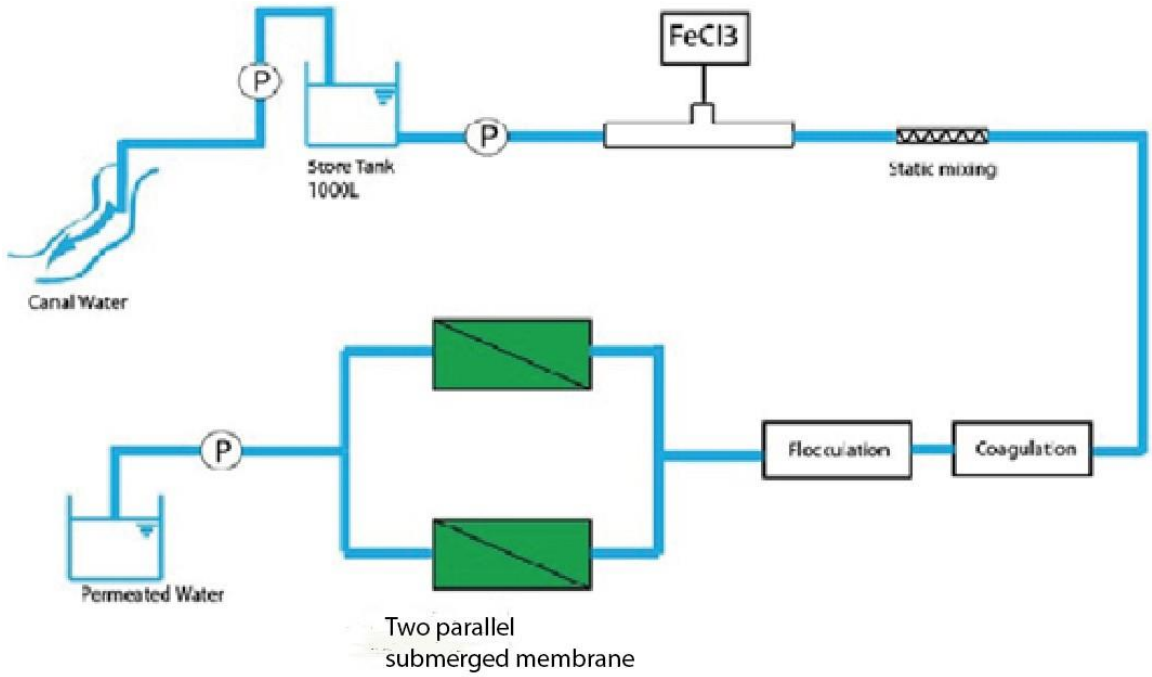

Figure 11: Experiment flow sketch

3.2.2 Measurements

3.2.2.1 Micro-pollutants measurement

The permeate water samples for four different situations(atrazine removed by SA SUPER and SA SUPER G, sulfamethoxazole removed by SA SUPER and SA SUPER G) were taken after every hour during the entire operational time (12 hour). Totally, there were 48 samples taken. The samples were stored in a fridge before measurement.

An ELISA kit was used for the measurement of the concentration of micro-pollutants. The ELISA kit is an immunoassay for the quantitative and sensitive detection of micro-pollutants in water samples. The test is based on the recognition of atrazine and sulfamethoxazole by specific antibodies. Micro-pollutants present in the sample and an enzyme-conjugate compete for the binding sites of the antibodies immobilized on the plate. After a washing step and the addition of the substrate solution a color signal is produced. The

intensity of the blue color is inversely proportional to the concentration of micro-pollutants present in the sample. The color reaction is stopped after a specified time and the color is evaluated using an ELISA reader (Fig. 12). For the measurement with the ELISA photometer, a wavelength of 450nm was used.

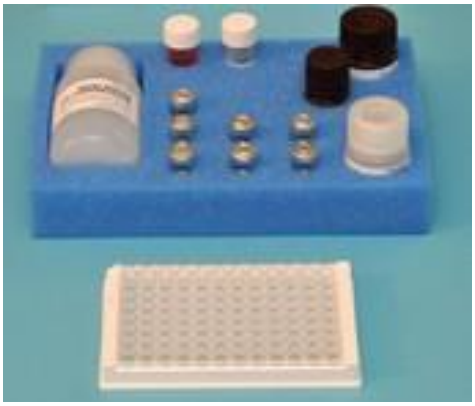

Figure 12: ELISA reader (http://www.abraxiskits.com/products.php)

3.2.2.2 Zeta potential measurement

To investigate the charge impact on the micro-pollutant adsorption capacity, the surface charge of the NOM-PAC layer outside of membrane was measured. The value of the zeta potential can present the charge capacity, which was measured with a Zetasizer Nano (Malvern)(Fig. 13).

Figure 13: Zetasizer Nano (http://www.bioresearchonline.com/doc/Zetasizer-Nano-0001)

Zetasizer Nano can only measure the sample in the liquid phase, so the sample contained the solution after the flocculation step and the pre-coated PAC that was scraped from the membrane. Before the measurement, the sample was shaken for a while to avoid PAC settling.

To make a comparison, two additional situations were analyzed. One of them was the same as in the membrane experiment but without Fe3+ dosing. The other one used demi-water as the inflow water source, so without NOM and flocs.

3.3 Micro-pollutants removal efficiency in different parts of the system

PAC is the major treatment step for the micro-pollutants removal in the system. The purpose of this experiment was to prove that indeed the PAC process is the only treatment step that removes micro-pollutants in the system. The setup is the same as in the membrane experiment and samples were taken after each individual treatment step (red point in Fig 14). After the coagulation/flocculation step, two different tracks of membranes was installed (one pre-coated with PAC another without PAC) to investigate the performance of the with PAC pre-coated membrane. The sample of the effluent was taken every hour during the whole operational period (8 hours) and the measurement methods were the same as in the membrane experiment. To prevent the influence of flocs, the sample taken after the coagulation and flocculation step were filtered through a 0.45µm filter.

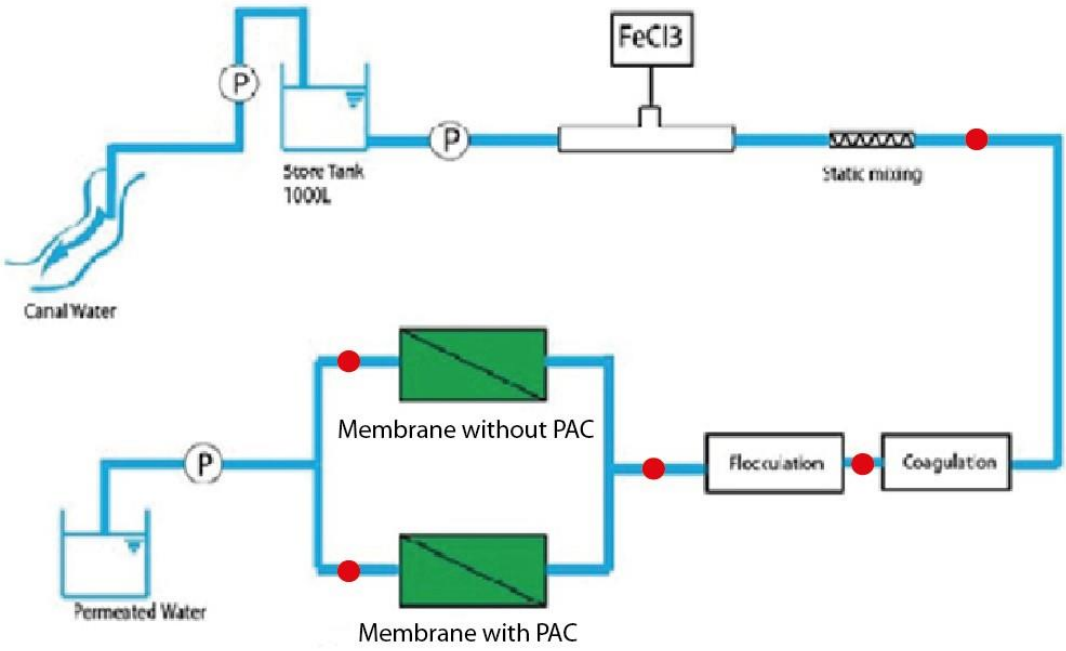

Figure 14: Samples point of the experiment system

3.4 Batch experiment

With batch experiments, the Freundlich constant K and n, as well as the kinetics parameter k_2 were determined under ideal conditions (equilibrium for the Freundlich constants and ideal kinetics for the kinetics parameter). The PAC and the micro-pollutants were the same as in the membrane experiment.

3.4.1 Freundlich constants (K, n)

Different amounts of PAC (0.001g, 0.005g, 0.01g, 0.02g, 0.03g and 0.04g) were dosed to six bottles with a volume of 10L canal water (Fig. 15). Micro-pollutant (concentration is 2µg/L) was added to each bottle

and stirred continuously during 48 hours to reach equilibrium. After 48 hours stirring, the remaining equilibrium concentrations were measured in each bottle. The measurement of the equilibrium concentration is the same as in the membrane experiment.

Figure 15: Freundlich constants experimental set up

3.4.2 Kinetic constant (k_2)

For modeling purposes, the mass transfer coefficient k_2 also needed to be determined. Parameter k_2 depends on the character of adsorbate and the type of carbon. In the experiment, a 10 liter bottle was filled with canal water and 2µg/l micro-pollutant solution was dosed to mixing bottle which contained 0.01g PAC. Several samples were taken after different periods of time (0.25h, 0.5h, 0.75h, 1h, 1.5h, 2h, 3h, 4h, 5h, 6h, 24h, 48h). The measurement of micro-pollutant concentration is the same as in the membrane experiment.

3.5 Modeling simulation

For the modeling part, Stimela was applied, in this case the Internet version (www.Stimela.com). The input of the models is water flow, water quality, and operational and process parameters. Water flow, micro-pollutants concentration, membrane surface area and PAC grain size was directly obtained from the experiment. The value of Freundlich constants (K, n) and Kinetic constant (k_2) were obtained from the batch experiment. Bed height and porosity were calculated as shown in section 4.4.3.

4. Results and discussion

4.1 Pre-coating experiment

The pre-coating experimental setup is presented in the previous chapter (section 3.1). The results of the pre-coating, with SA SUPER and SA SUPER G PAC, on the membrane are presented in Fig. 16 and Fig. 17. On the vertical axis in the graph is the final PAC density on the membrane after the pre-coating experiment and on the horizontal axis is the PAC dosage in the mixing tank before the experiment.

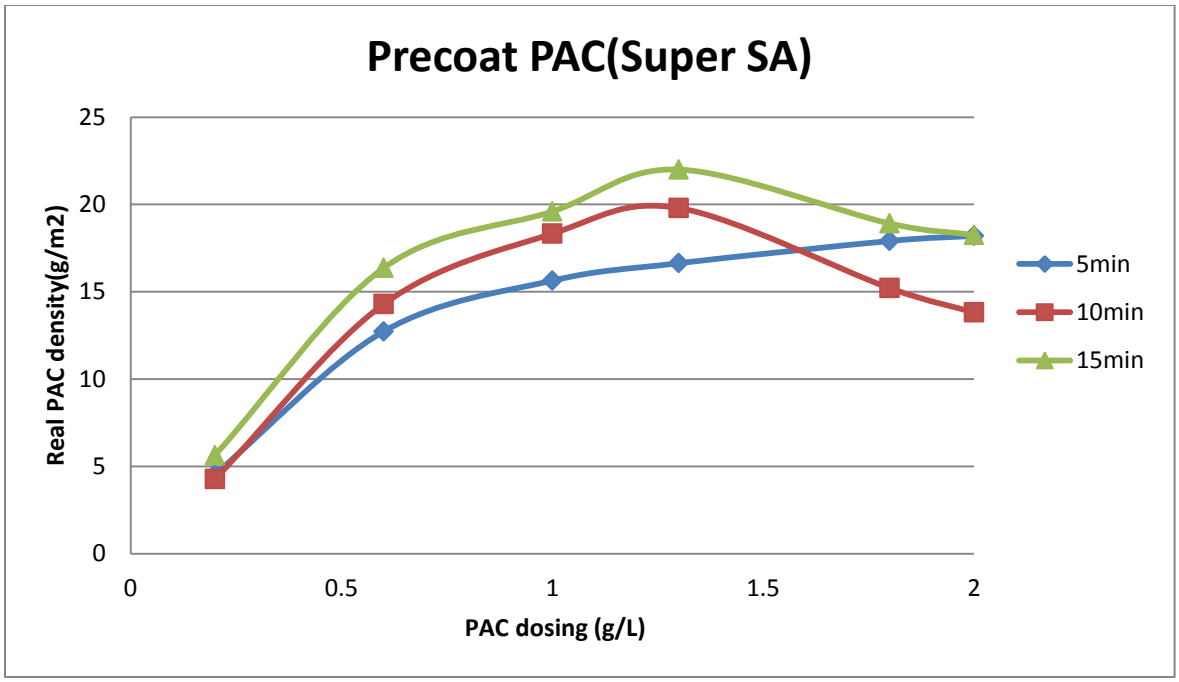

Figure 16: Pre-coating PAC capacity result (Super SA)

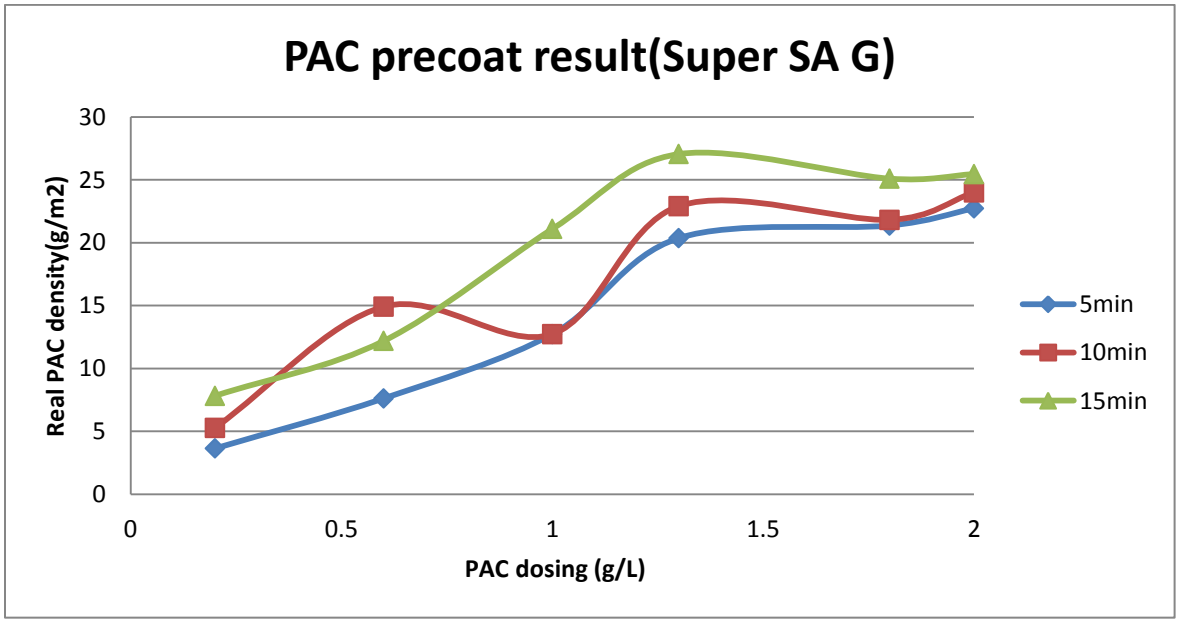

Figure 17: PAC pre-coating capacity result (Super SA G)

As we can see from the results, the pre-coating capacity increased with stirring times and the maximum pre-coating capacity occurred after 15 minutes of stirring time for the different PAC dosing values. In addition it can be seen that the larger sized PAC is easier to be used for pre-coating on the membrane than the smaller one. The maximum amount of pre-coating capacity for SUPER SA and SUPER SA G was $22g/m^2$ and $27g/m^2$ respectively. To guarantee uniform experimental conditions for the different PACs in the experiment, the same amount of PAC was chosen as the target pre-coating value. So for both PACs the smaller pre-coating amount of $22g/m^2$ was chosen during the membrane experiment. This means

that 1.3g/L SUPER SA and 1g/L SUPER SA G was dosed in the mixing tank and the stirring time was 15 minutes. The real amount of pre-coated PAC was checked during every experiment.

4.2 PAC-Membrane filtration results

Four groups of experiments (atrazine removed by SA SUPER, atrazine removed by SA SUPER G, sulfamethoxazole removed by SA SUPER, sulfamethoxazole removed by SA SUPER G) were designed to determine the performance of different sizes of PAC to remove the two different micro-pollutants. As mentioned before, the real pre-coating value of PAC on the membrane was checked during the membrane experiment and the results for the four different situations were around 22g/m^2 which were not much different from the results during the pre-coating experiments. Therefore, for the sake of convenience for later calculation and modeling, the PAC density was assumed to be constant at 22g/m^2. The results of the membrane experiments are shown in Fig. 18. The analyses of the results were done on two aspects:

1) The mechanism of a certain micro-pollutant removed by different PACs (section 4.2.1)
2) The mechanism of a certain PAC removing different micro-pollutants (section 4.2.2).

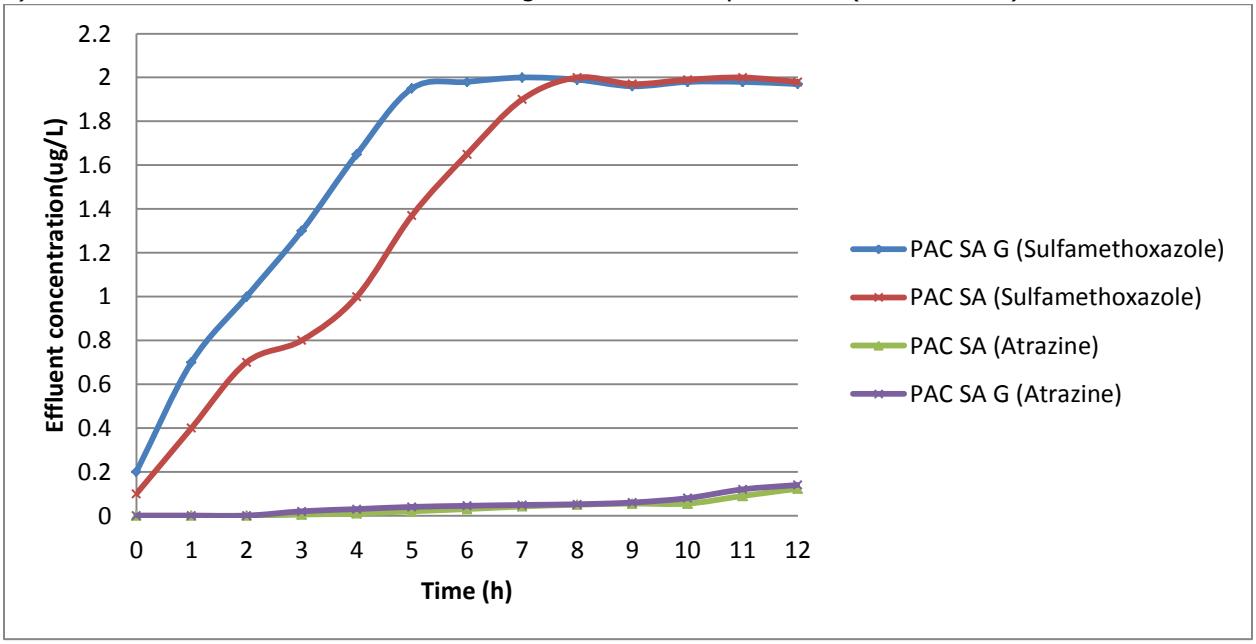

Figure 18: Breakthrough curve of atrazine and sulfamethoxazole removed by different PAC

4.2.1 Micro-pollutant removal by different PACs

Several factors can influence the micro-pollutant removal efficiency by PAC, such as the PAC pore size, charge and the hydrophobic/hydrophilic character of the activated carbon.

According to the results (Fig. 18), the smaller size of PAC presented a slower breakthrough trend than the larger PAC particle size for both atrazine and sulfamethoxazole removal. For the atrazine removal, although the PAC was not totally saturated within the operational time, after 12 hours, the effluent concentration was 0.12μg/L for the 5μm PAC particle size and 0.14μg/L for the 21μm particle size,

respectively. While for sulfamethoxazole, the total breakthrough occurred after 5 hours for the larger PAC size and breakthrough of the smaller size of PAC was delayed to 8 hours.

The two kinds of PACs were the same brand and only had different in sizes, so the charge and hydrophilic/hydrophobic character should be similar. This means that those two characters are not the major influencing factors, and the difference in the micro-pollutants breakthrough line was mainly because of the difference in the total surface area between the two activated carbons, which in its turn is the result of difference in particle size. The total surface area for the two PAC are 1150m^2/g (SA Super) and 1100m^2/g (SA Super G) respectively(Table 3), which means that the surface areas were 2530m^2 and 2420m^2, respectively. As a result, the smaller sized PAC had a slower breakthrough compared to the larger sized PAC.

4.2.2 Different micro-pollutant removal efficiencies by the same PAC

Fig. 18 also represents the removal efficiency of different micro-pollutants removed by the same PAC. It indicates that the sulfamethoxazole showed a faster breakthrough than atrazine. According to(de Ridder, Villacorte et al. 2010), three factors influence the removal efficiency of different micro-pollutants, removed by PAC, which are the size(molecular weight), charge and hydrophobic/hydrophilic character of the micro-pollutants.

The molecular weight of atrazine is 215.7 g/mol and of sulfamethoxazole is 253.279 g/mol, which is not too different. (de Ridder, Villacorte et al. 2010) also showed that the particle size of a micro-pollutant is not the dominant factor influencing the micro-pollutant removal by activated carbon. In addition, (de Ridder, Villacorte et al. 2010) concluded that if the raw water is organic-free, the charge of the micro-pollutant does not impact much on the micro-pollutant removal efficiency. However, in this case, the inflow water was surface water which contains natural organic matter (NOM), fouling the activated carbon (see Fig.19). The charge of the NOM- PAC layer was measured during the whole experiment and the results illustrated that the NOM-PAC layer was negatively charged (Table 7), which can lead to charge repulsion of negatively charged solutes. In this case the sulfamethoxazole (pKa=5.8) showed a more negative charge than the atrazine (neutrally charged, pKa=1.7), so sulfamethoxazole is easier repulsed by the PAC-NOM layer and more difficult to adsorb on PAC.

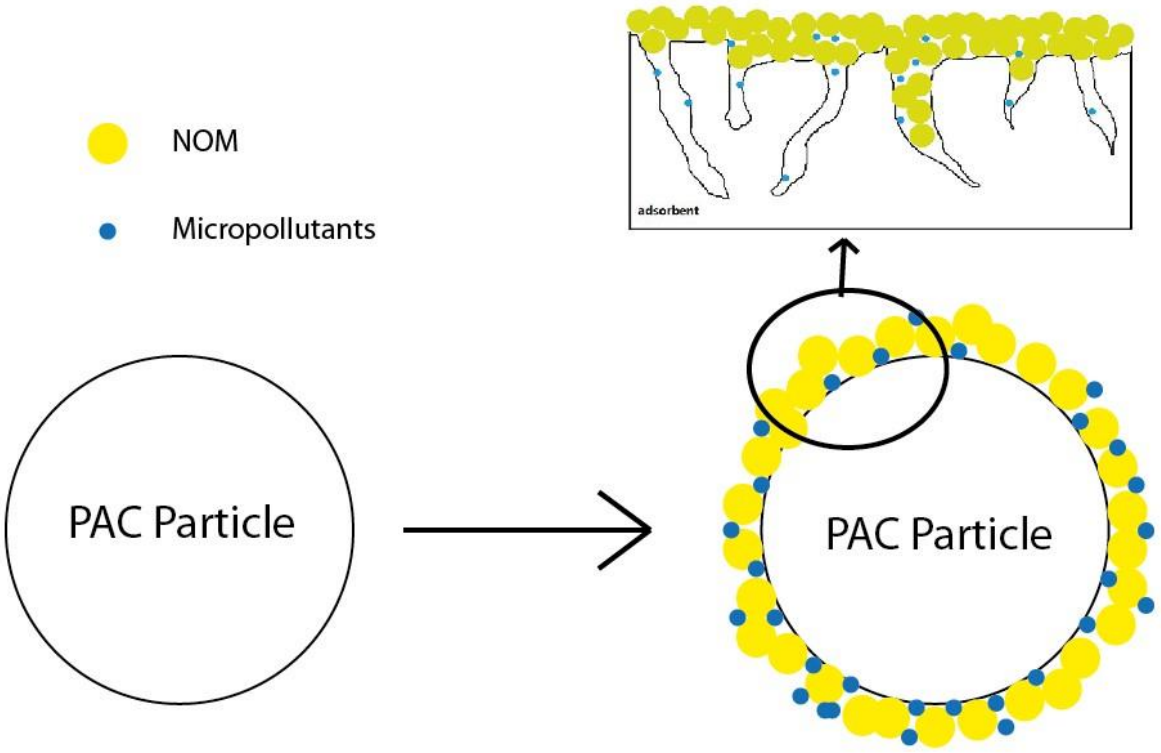

Figure 19: NOM-PAC layer layout

Table 7: Zeta potential value of NOM-PAC layer during the experiment time

Time	Zeta potential (canal water with Fe3+ dosing)	Zeta potential value (canal water without Fe3+ dosing)	Zeta potential (demi-water)
1	-14.3	-10.8	-9.8
2	-14	-11.1	-10.2
3	-14.2	-11.5	-10.1
4	-13.9	-12	-9.9
5	-13	-11.6	-11
6	-13.4	-13.4	-10.4
7	-14.3	-10.4	-9.3
8	-13.8	-11	-9.8
9	-15.2	-11.9	-10
10	-13.8	-11.4	-11.2
11	-14	-10.5	-10
12	-14	-11.7	-10.5

From Table 7, the zeta potential values for the different operational conditions are presented. As we can see, in all three experiments, the zeta potential was more or less at a constant value during the whole operational period and all the results show a negative value, which means that the PAC layer in those three scenarios were negatively charged.

However, in the left column of the table, the absolute value is the largest, which means that in the membrane experiment with canal water containing flocs, the NOM-PAC layer had the maximum negative charge. Without the influence of flocs the NOM-PAC layer shows a lower negative charge than in the situation with the influence of the flocs. The right column is the demi-water experiment without Fe^{3+} dosing. The results illustrate that the negative charge in this case is the lowest one.

Moreover, the hydrophobic/hydrophilic character of the two target micro-pollutants is quite different. Sulfamethoxazole (log Kow 0.89) is more hydrophilic than atrazine (log Kow 2.61), which indicates that the hydrophobic/hydrophilic character can be another factor leading to the different breakthrough curve of the micro-pollutants.

4.3 Removal efficiency in different steps

An additional experiment was designed to indicate which step is the most important micro-pollutant removal step in the coagulation/flocculation-PAC-MF system. The results of the concentration of atrazine are presented in Table 8.

Table 8: Atrazine concentration after different treatment steps

Time (h)	Inflow (µg/L)	Coagulation (µg/L)	Flocculation (µg/L)	PAC- membrane (µg/L)	Membrane (µg/L)
1	1.98	1.8	1.77	0	1.75
2	1.95	1.72	1.82	0	1.83
3	2.02	1.79	1.75	0	1.68
4	1.96	1.83	1.69	0	1.64
5	1.98	1.73	1.75	0.1	1.7
6	1.99	1.77	1.81	0.13	1.78
7	1.97	1.82	1.78	0.18	0.74
8	1.98	1.79	1.72	0.23	1.72

From Table 8, it can be observed that the additional experiment lasted 8 hours and the inflow of atrazine concentration was stable at 2µg/L. The results indicated that the atrazine concentration after the coagulation and flocculation step was not changing much, so the removal efficiency for those two steps was extremely limited. For the condition of a flow through membrane alone, the concentration was still the same as the previous step. While for the water flow through the PAC-membrane system, the micro-pollutant concentration decreased to 0 in the beginning. After that the effluent concentration increased because the PAC began to break through. From above analysis, we can conclude that the PAC played a leading role in the micro-pollutant removal, which was to be expected.

4.4 Modeling results

4.4.1 K, n and k_2 result

Freundlich constants (K, n)

The results of the calibration of the Freundlich constants are presented in Table 9. As we can see, the results in the four situations were different, but for the same micro-pollutant they were similar. For the

convenience of later calculations and computer modeling, the Freundlich constants were assumed to be the same per micro-pollutant, see Table 10.

Table 9: Result of batch experiment for Freundlich constants

	n	K ((g/kg)*(m^3/g)^n)
SA Super(5) (atrazine)	0.8572	55
SA Super G(21) (atrazine)	0.8055	49
SA Super(5) (Sulfamethoxazole)	1.03	23
SA Super G(21) (Sulfamethoxazole)	1.0102	21

Table 10: Result of batch experiment for Freundlich constants after adjustment

	n	K ((g/kg)*(m^3/g)^n)
SA SUPER (atrazine)	0.8243	55.6
SA SUPER G (atrazine)		
SA SUPER (sulfamethoxazole)	1.0122	22.3
SA SUPER G (sulfamethoxazole)		

The theoretical value for Freundlich n should be from 0 to 1, so the n-value for sulfamethoxazole situation is a little higher than the empirical value. For the value of Freundlich K, the more hydrophobic micro-pollutant (atrazine) had a higher value than the hydrophilic micro-pollutant (sulfamethoxazole) (more than two times higher).

Kinetic constant (k_2)

Concentrations after different time intervals were measured (Table 11). The obtained results were plotted in graphs to represent the kinetics of PAC adsorption (Fig. 20). By using Equ 4, and fitting the measured curves to the calculated curves, the k_2 value was derived. The results of different scenarios are presented in Table 12.

Table 11: Result of batch experiment

Time(h)	Effluent concentration(µg/L)	Calculated curve(µg/L)	k_2 (1/h)
0	2.00	2.00	0.6
0.25	1.87	1.90	
0.5	1.72	1.82	
0.75	1.68	1.74	
1	1.61	1.68	
1.5	1.55	1.58	
2	1.49	1.50	
3	1.43	1.41	
4	1.35	1.35	
5	1.31	1.33	
6	1.29	1.31	
24	1.29	1.29	

48	1.29	1.29	

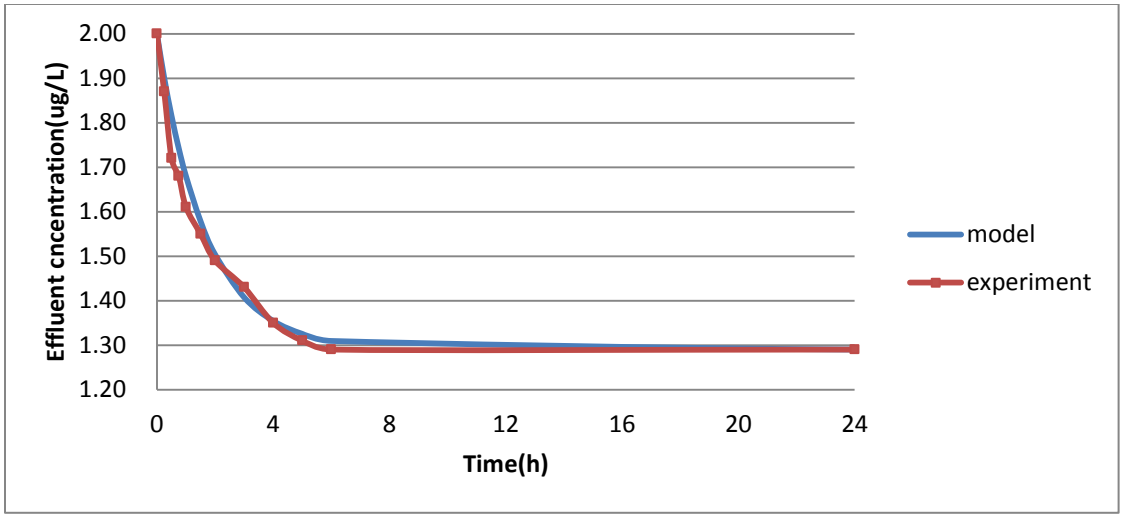

Figure 20: Modeling and experiment kenetic line for k_2 value

Table 12: Batch experiment result

	k_2 (1/h)
SA SUPER (atrazine)	0.7
SA SUPER G (atrazine)	0.6
SA SUPER (sulfamethoxazole)	0.5
SA SUPER G (sulfamethoxazole)	0.4

From Table 12 it can be concluded that the $k_2$values did not show the increase with decreasing PAC particle size as expected from section 2.6.3. The k_2 values for both PACs were almost the same. This is probably because during the batch experiments, the PAC particles were not well stirred and some particles could stick together, influencing the adsorption capacity (Fig. 21). On top of that, another probable reason is that a water layer is formed outside the PAC particle in the batch experiment, also influencing the adsorption rate of the micro-pollutants.

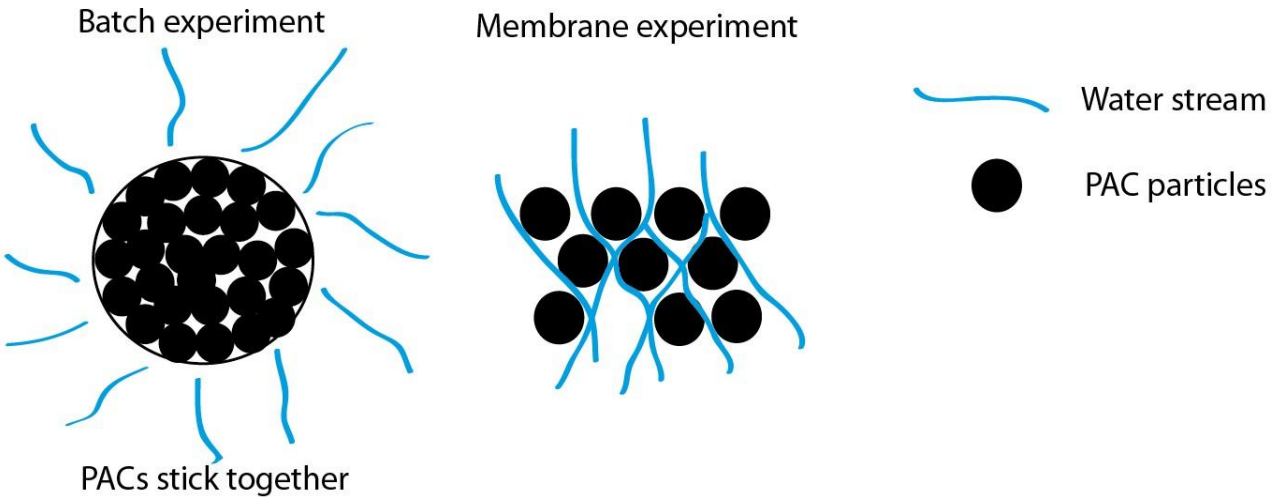

Figure 21: Different adoption mechanism for batch and membrane experiment

4.4.2 Modeling result

Stimela was used as introduced in section 2.6.1. From the above batch experiments, the kinetic value for different PAC particles was quite different from the theoretical relationship.

For the membrane experiment a different approach was followed and the modeling results were compared to the experimental results (Fig. 22 and Fig. 24). The K and n-values obtained from the batch experiments were used (Table 10), and the k_2 value was increased by a factor 4 for the smaller PAC particle situation (Table 13). The dotted breakthrough line was obtained from the membrane experiment, and the straight line is the result from modeling.

Table 13: k_2 value according to the empirical equation

	Super SA (5µm)	Super SA G (21µm)
Atrazine	2.4	0.6
Sulfamethoxazole	2	0.5

From Fig. 22, the PAC breakthrough curve was simulated according to different k_2 value obtained from section 2.6.3. In the beginning, the modeling curve did not match the experimental curve very well, which is probably because the PAC pre-coating layer is not uniform along the membrane surface. While as the experiment went on, the influence of PAC thickness became smaller, so the variability became smaller, especially after 10 hours operation time. The trend of the modeling result is similar to the trend of the breakthrough line obtained from the experiment.

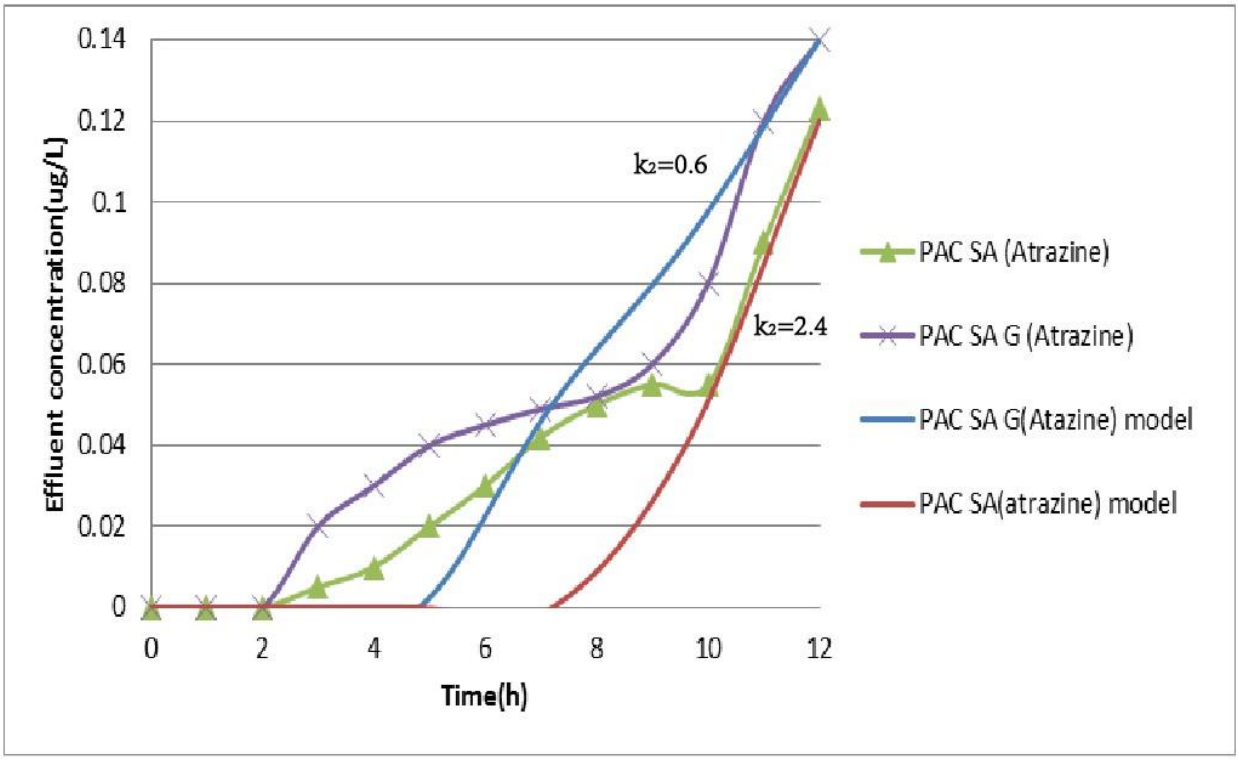

Figure 22: Experiment and modeling breakthrough line for atrazine under two different PAC dosage

It should be considered that the vertical range in Fig. 22 is from 0µg/L to 0.14µg/L, while the inflow of micro-pollutants concentration is 2 µg/L. To better understand the PAC performance, a longer operational time was simulated which is shown in Fig 23.

In Fig 23, the operational time is prolonged to 48 hours. In the beginning, the smaller PAC breaks through later than the larger one, which is the same as in the results of the membrane experiment, while, after certain time, the smaller PAC will breakthrough faster than the larger PAC, and finally there is an intersection point. This is because the K, n value is the same for the same micro-pollutant. The smaller and larger PAC breakthrough lines must meet somewhere and the areas between the two lines should be same in the left and right area of the intersection point.

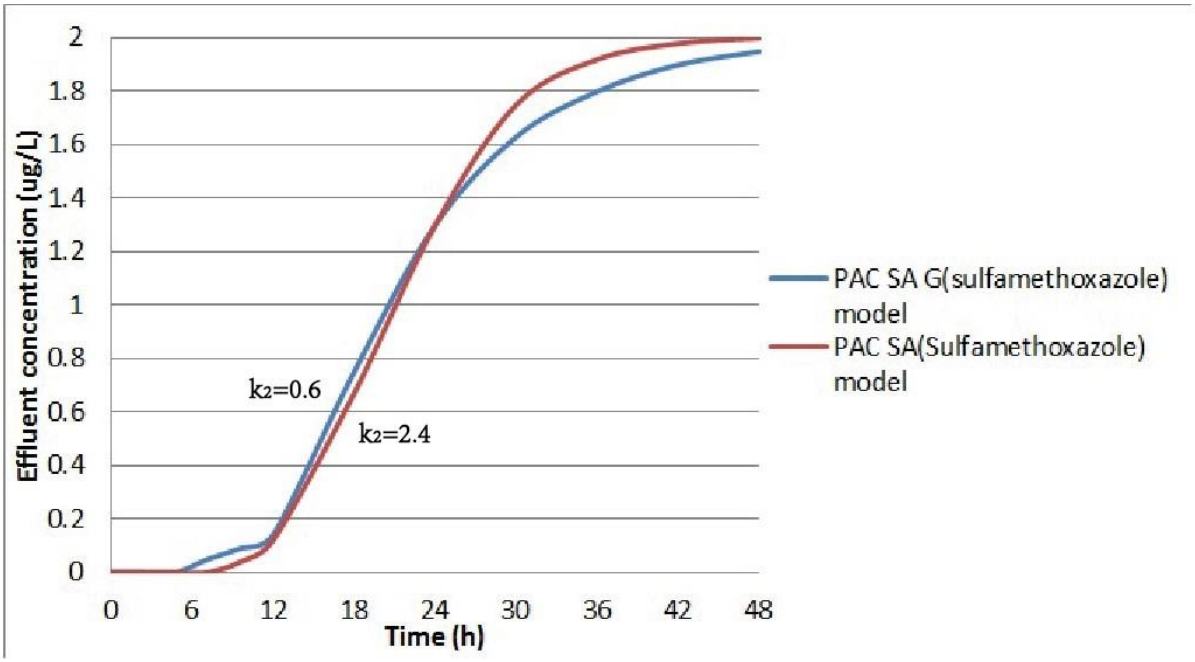

Figure 23: PAC breakthrough of sulfamethoxazole removal after a long time model

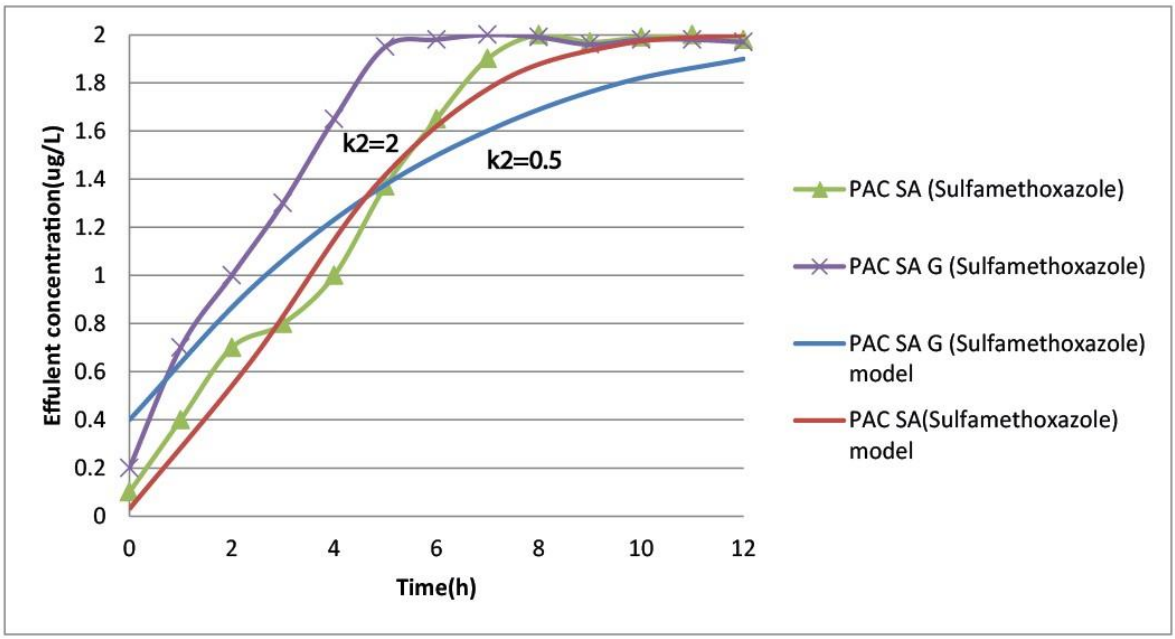

Figure 24: Experiment and modeling breakthrough line for sulfamethoxazole under two different PAC dosages

In Fig. 24 the experimental results and modeling results for the small PAC particle sizes are rather similar, but for the large sized PAC, the blue modeling line should have been higher to match the experimental results, which means that the k_2 value in sulfamethoxazole with SUPER SA should be increased to 0.8 or even 1 1/h.

4.4.3 Sensitive analysis

In this part, different input parameters to Stimela were adjusted and the results illustrate which parameter is the most important factor to influence the breakthrough line. The analysis was divided into two parts: calibration parameters and operational input parameters.

For the simulation we use the Freundlich isotherm and the kinetic constant k_2 obtained from the batch experiments. For other parameters, Grain size is 0.005mm and mass density of the activated carbon under dry condition is 370kg/m³. For the rest of the parameters the calculation steps are shown below

Flow though membrane:

$$Q = \text{flux} * A \tag{9}$$

Where:
Q: Flux though the membrane (l/m^2*h)
A: Membrane area

Bed height

$$H = \frac{M}{\rho * A} \tag{10}$$

Where:
H: Bed height (m)
M: Mass of PAC preload on membrane (g)
ρ: Mass density of the activated carbon in wet condition (kg/m³)

Filter porosity

$$p = \frac{V_{wet} - V_{pore(wet)}}{V_{dry} - V_{pore(dry)}} \tag{11}$$

Where
P: Filter porosity (%)
V_{wet}: Volume of PAC in wet condition (m^3)
$V_{pore(wet)}$: Volume of pore between PAC particles in wet condition (m^3)
V_{dry}: Volume of PAC in wet condition (m^3)
$V_{pore(wet)}$: Volume of pore between PAC particles in dry condition (m^3)

Calibration parameters

The constants K, n and k_2 values, that cannot be changed by operational staff, only depend on the character of the PAC. As an example, we chose the scenario where sulfamethoxazole was removed by the

large sized PAC. The result of this case was already shown in Fig. 24, and presented again in Fig. 25. The purple line in Fig. 25 is the experimental result and the blue line is the modeling line with the original batch experimental result. All the other input data for Stimela are shown in Table 14. As we explained in section 4.4.2, the k_2 value can be increased to obtain a better match, so the k_2 value was increased to 0.8 1/h and the red line was obtained, which is a better match to the experimental results than the blue curve. After that, the influence of the K value was indicated, the K value was decreased to 18 $(g/kg)*(m^3/g)^n$, and the black curve was obtained, which is the most optimal curve to match the experimental data.

So the optimal k_2 value for large PAC removing sulfamethoxazole can be 0.8 1/h and the K value is 18 $(g/kg)*(m^3/g)^n$. In addition, the increase of k_2 value can make the breakthrough slower and the decrease of the K value can accelerate the PAC breakthrough in Stimela.

Table 14: Input data in Stimela

Parameter	unit	value
Flow	m^3/h	0.0066
Micro-pollutant concentration	mg/l	0.002
Filter surface area	m^2	0.11
Bed height	m	0.000055
Grain size	mm	0.005
Filter porosity	%	44
Freundlich constant n		1
Mass density of the activated carbon	kg/m^3	370
Freundlich constant K	$(g/kg)*(m^3/g)^n$	22.3
Mass transfer coefficient k_2	1/h	0.5
Number of completely mixed reactors		5

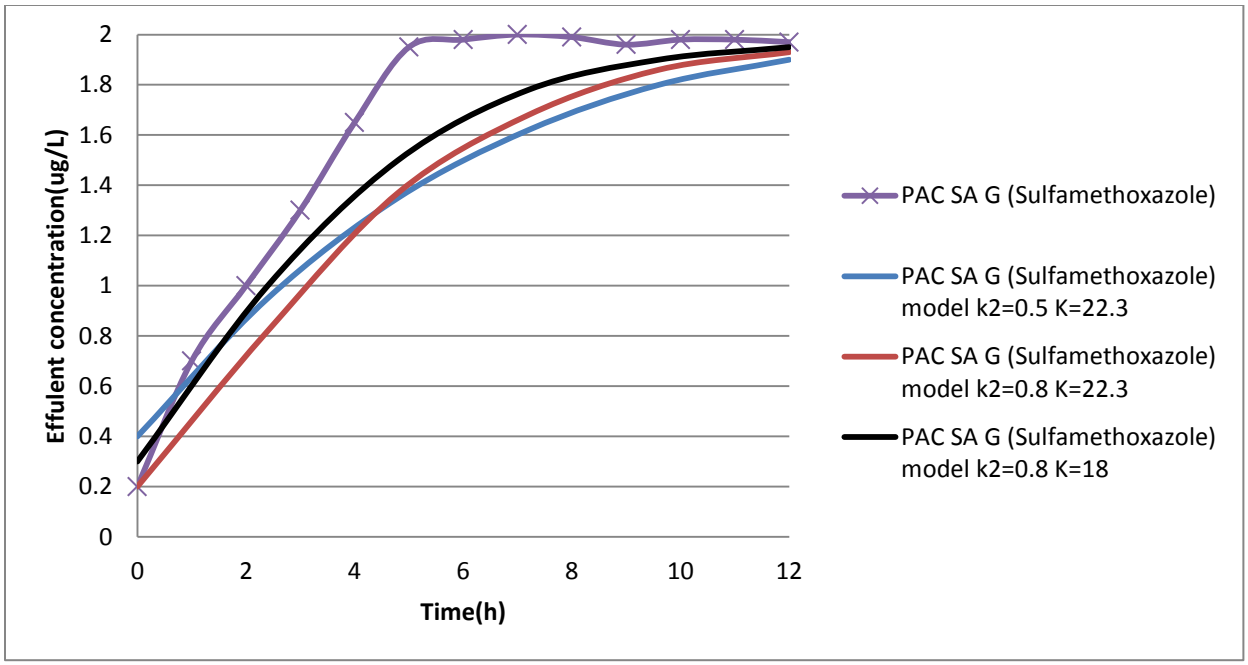

Figure 25: Breakthrough curve with initial input data

Operational input analysis

There are also some operational parameters for the Stimela input, such as flow, micro-pollutant concentration and pre-coating layer thickness. From the simulation of Stimela, the increase of flow and micro-pollutant concentration will accelerate the PAC breakthrough, while for the thickness of the PAC layer, the breakthrough happened later. All the influences of the input for Stimela are shown in Table 15.

Table 15: The most influence factor for micro-pollutants removal

Parameter	Increase	Influence level
Flow	Accelerated effect	large
Micro-pollutant concentration	Accelerated effect	large
Bed height	Delayed effect	large
Freundlich constant K	Delayed effect	large
Mass transfer coefficient k_2	Delayed effect	small

5. Conclusions and recommendations

5.1. Conclusions

From the experiments and the modeling, performed in this research, the following conclusions can be drawn for a PAC – membrane filtration system:

- For the same brand of PAC, breakthrough occurred later for smaller particle sizes, which is due to different k_2 values.
- The breakthrough for the more hydrophilic micro-pollutant (sulfamethoxazole log Kow 0.89) happened faster than for the more hydrophobic micro-pollutant (atrazine log Kow 2.61). On top of that, sulfamethoxazole showed a more negative charge compared to the atrazine,

leading to charge repulsion by the NOM-PAC layer on the membrane (also showing a negative charge).

- Stimela can model the breakthrough line with certain input information. After some adjustments, it was found that some parameters such as PAC height, Freundlich constant n, Freundlich constant K can have an impact on the breakthrough line.

5.2. Recommendations

The concentration of PAC dosing in the system is calculated below:

Dosing concentration = $\frac{mass\ of\ PAC\ dosing\ in\ the\ system}{water\ flow\ through\ the\ system}$ = 2.5g/(60L/(h*m^2)*0.11m^2*12h) = 0.03g/L

Using the same method presented above, the PAC concentration after 6 and 24 hours of operation can be calculated, the results are shown in table 16.

Table 16: Performance for the system under different operational time

Operational time	6	12	24	remark
Volume of treatment water (L)	39.6	79.2	158.4	
PAC dosing (g/L)	0.06	0.03	0.015	
Atrazine removal percentage	99%	95%	50%	SA Super
Atrazine removal percentage	99%	95%	40%	SA Super G
Sulfamethoxazole removal percentage	20%	0		SA Super
Sulfamethoxazole removal percentage	5%	0		SA Super G

5.2.1 Particle size

According to the Table 16, for the atrazine removal the different size of PAC have not too much removal difference in the beginning of the experiment. While the operational time increased, the difference occurred, but the value is not huge (only 10% different in 24 hours). So for the atrazine removal in this case, the larger particle size of PAC (SA SUPER G) is a better option because of the lower price.

While for the sulfamethoxazole removal, the removal capacity is extremely low within even short operational time (20% for small PAC and 5% for large one) for both size of PAC, so those two kinds of PAC are not an optimal choice for sulfamethoxazole removal in this case. However, if there is an emergency situation which SA SUPER PAC has to apply, the smaller size of PAC is a better option.

5.2.2 Operational time

The percentage of micro-pollutants removal can be got from the filtration result (Fig. 18). As we can see, the atrazine removal ratio is rather high within 12 hour for both PAC particle size, to continue check the PAC performance in longer time, 24 hour operational time was simulated by Stimela and the results shown that the removal efficiency of atrazine by Super and SA SUPER G is 50% and 40% respectively. While for the sulfamethoxazole, the removal efficiency is rather low, but if the running time decreased half, the percentage of micro-pollutants removal will double. The 24 hour scenario is not simulated in this case, because the performance of PAC is quite disappointing, so it would be strongly recommended that do not manage the PAC-microfiltration system to remove sulfamethoxazole for a long time.

5.2.3 Operational situation

From section 4, different influence factors were investigated. The result showed that, for those parameter related to operational situation, the total inflow, micro-pollutants concentration and thickness of PAC layer are the important influence factors for the breakthrough line.

List of References

Acero, J. L. and U. Von Gunten (2001). "Characterization of oxidation processes: Ozonation and the AOP O 3/H 2O 2." Journal / American Water Works Association **93**(10): 90-100.

Adham, S. S., V. L. Snoeyink, et al. (1993). "Predicting and verifying TOC removal by PAC in pilot-scale UF systems." Journal / American Water Works Association **85**(12): 58-68.

Adham, S. S., V. L. Snoeyink, et al. (1991). "Predicting and verifying organics removal by PAC in an ultrafiltration system." Journal / American Water Works Association **83**(12): 81-91.

Agenson, K. O. and T. Urase (2007). "Change in membrane performance due to organic fouling in nanofiltration (NF)/reverse osmosis (RO) applications." Separation and Purification Technology **55**(2): 147-156.

Belloni, V., F. Dessì-Fulgheri, et al. (2011). "Early exposure to low doses of atrazine affects behavior in juvenile and adult CD1 mice." Toxicology **279**(1–3): 19-26.

Benachour, N., S. Moslemi, et al. (2007). "Cytotoxic effects and aromatase inhibition by xenobiotic endocrine disrupters alone and in combination." Toxicology and Applied Pharmacology **222**(2): 129-140.

Carter, M. C. and W. J. Weber Jr (1994). "Modeling adsorption of tce by activated carbon preloaded by background organic matter." Environmental Science Technology **28**(4): 614-623.

Cerejeira, M. J., P. Viana, et al. (2003). "Pesticides in Portuguese surface and ground waters." Water Research **37**(5): 1055-1063.

Chang, Y. and M. M. Benjamin (1996). "Iron oxide adsorption and UF to remove NOM and control fouling: Addition of iron oxide particles to a UF system can significantly increase NOM removal efficiency, slowing membrane fouling." Journal / American Water Works Association **88**(12): 74-88.

Chang, Y. J., K. H. Choo, et al. (1998). "Combined adsorption-UF process increases TOC removal." Journal / American Water Works Association **90**(5): 90-102.

Choi, Y. H., H. S. Kim, et al. (2008). "Role of hydrophobic natural organic matter flocs on the fouling in coagulation-membrane processes." Separation and Purification Technology **62**(3): 529-534.

Chu, W. and C.-W. Ma (2000). "Quantitative prediction of direct and indirect dye ozonation kinetics." Water Research **34**(12): 3153-3160.

Cornelissen, E. R., N. Moreau, et al. (2008). "Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions." Water Research **42**(1–2): 413-423.

Cotruvo, J. A. (1985). "Organic micropollutants in drinking water: An overview." Science of The Total Environment **47**(0): 7-26.

de Ridder, D. J., L. Villacorte, et al. (2010). "Modeling equilibrium adsorption of organic micropollutants onto activated carbon." Water Research **44**(10): 3077-3086.

Ebie, K., F. Li, et al. (1995). "Effect of pore size distribution of activated carbon on the adsorption of humic substances and trace organic compounds." Water Supply **13**(3-4): 65-70.

Fabris, R., E. K. Lee, et al. (2007). "Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes." Journal of Membrane Science **289**(1–2): 231-240.

Fan, W. Q., T. Yanase, et al. (2007). "Atrazine-induced aromatase expression is SF-1 dependent: Implications for endocrine disruption in wildlife and reproductive cancers in humans." Environmental Health Perspectives **115**(5): 720-727.

Franz, M., H. A. Arafat, et al. (2000). "Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon." Carbon **38**(13): 1807-1819.

Gabriel, F. L. P., E. J. Routledge, et al. (2008). "Isomer-specific degradation and endocrine disrupting activity of nonylphenols." Environmental Science and Technology **42**(17): 6399-6408.

Gai, X.-J. and H.-S. Kim (2008). "The role of powdered activated carbon in enhancing the performance of membrane systems for water treatment." Desalination **225**(1–3): 288-300.

Gillogly, T. E. T., V. L. Snoeyink, et al. (1998). "14C-MIB adsorption on PAC in natural water." Journal / American Water Works Association **90**(1): 98-108.

Giusi, G., R. M. Facciolo, et al. (2006). "The endocrine disruptor atrazine accounts for a dimorphic somatostatinergic neuronal expression pattern in mice." Toxicological Sciences **89**(1): 257-264.

Graziano, N., M. J. McGuire, et al. (2006). "2004 National atrazine occurrence monitoring program using the abraxis ELISA method." Environmental Science and Technology **40**(4): 1163-1171.

Guo, W. S., S. Vigneswaran, et al. (2005). "Effect of flocculation and/or adsorption as pretreatment on thecritical flux of crossflow microfiltration." Desalination **172**(1): 53-62.

Guo, W. S., S. Vigneswaran, et al. (2004). "Experimental investigation of adsorption–flocculation–microfiltration hybrid system in wastewater reuse." Journal of Membrane Science **242**(1–2): 27-35.

Haberkamp, J., A. S. Ruhl, et al. (2007). "Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behaviour in ultrafiltration." Water Research **41**(17): 3794-3802.

Heberer, T. (2002). "Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data." Toxicology Letters **131**(1–2): 5-17.

Heijman, S. G. J., A. M. van Paassen, et al. (1999). "Adsorptive removal of natural organic matter during drinking water treatment." Water Science and Technology **40**(9): 183-190.

Howe, K. J., A. Marwah, et al. (2006). "Effect of Coagulation on the Size of MF and UF Membrane Foulants." Environmental Science & Technology **40**(24): 7908-7913.

Jones, O. A. H., N. Voulvoulis, et al. (2005). "Human pharmaceuticals in wastewater treatment processes." Critical Reviews in Environmental Science and Technology **35**(4): 401-427.

Kasaoka, S., Y. Sakata, et al. (1989). "Design of molecular-sieve carbon. Studies on the adsorption of various dyes in the liquid phase." International chemical engineering **29**(4): 734-742.

Katsoyiannis, I. A., S. Canonica, et al. (2011). "Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O3/H2O2 and UV/H2O2." Water Research **45**(13): 3811-3822.

Khan, M. M. T., S. Takizawa, et al. (2011). "Membrane fouling due to dynamic particle size changes in the aerated hybrid PAC–MF system." Journal of Membrane Science **371**(1–2): 99-107.

Kilduff, J. E., T. Karanfil, et al. (1998). "TCE adsorption by GAC preloaded with humic substances." Journal / American Water Works Association **90**(5): 76-89.

Kim, H.-C., J.-H. Hong, et al. (2006). "Fouling of microfiltration membranes by natural organic matter after coagulation treatment: A comparison of different initial mixing conditions." Journal of Membrane Science **283**(1–2): 266-272.

Kim, T. U., G. Amy, et al. (2005). Rejection of trace organic compounds by high-pressure membranes. **51:** 335-344.

Kimura, K., G. Amy, et al. (2003). "Adsorption of hydrophobic compounds onto NF/RO membranes: an artifact leading to overestimation of rejection." Journal of Membrane Science **221**(1–2): 89-101.

Kimura, K., G. Amy, et al. (2003). "Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes." Journal of Membrane Science **227**(1–2): 113-121.

Kimura, K., S. Toshima, et al. (2004). "Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes." Journal of Membrane Science **245**(1–2): 71-78.

Kiso, Y., T. Kon, et al. (2001). "Rejection properties of alkyl phthalates with nanofiltration membranes." Journal of Membrane Science **182**(1–2): 205-214.

Knappe, D. R. U., Y. Matsui, et al. (1998). "Predicting the capacity of powdered activated carbon for trace organic compounds in natural waters." Environmental Science and Technology **32**(11): 1694-1698.

Knappe, D. R. U., V. L. Snoeyink, et al. (1999). "Atrazine removal by preloaded GAG." Journal / American Water Works Association **91**(10): 97-109.

Lambert, S. D., N. J. D. Graham, et al. (1993). "Ozone degradation of selected non-agricultural herbicides." Ozone: Science and Engineering **15**(5): 457-464.

Lastoskie, C., K. E. Gubbins, et al. (1993). "Pore size distribution analysis of microporous carbons: A density functional theory approach." Journal of Physical Chemistry **97**(18): 4786-4796.

Lee, C. W., S. D. Bae, et al. (2007). "Application of ultrafiltration hybrid membrane processes for reuse of secondary effluent." Desalination **202**(1–3): 239-246.

Lee, S., J.-W. Lee, et al. (2009). "Removal of 17β-estradiol by powdered activated carbon—Microfiltraion hybrid process: The effect of PAC deposition on membrane surface." Journal of Membrane Science **326**(1): 84-91.

Li, L., P. A. Quinlivan, et al. (2002). "Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution." Carbon **40**(12): 2085-2100.

Li, Q., V. L. Snoeyink, et al. (2003). "Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight." Water Research **37**(20): 4863-4872.

Li, Y., X. Zhang, et al. (2011). "Effect of powdered activated carbon on immersed hollow fiber ultrafiltration membrane fouling caused by particles and natural organic matter." Desalination **278**(1–3): 443-446.

Libotean, D., J. Giralt, et al. (2008). "Organic compounds passage through RO membranes." Journal of Membrane Science **313**(1–2): 23-43.

Lin, C.-F., Y.-J. Huang, et al. (1999). "Ultrafiltration processes for removing humic substances: effect of molecular weight fractions and PAC treatment." Water Research **33**(5): 1252-1264.

Lin, Y.-L., P.-C. Chiang, et al. (2007). "Removal of small trihalomethane precursors from aqueous solution by nanofiltration." Journal of Hazardous Materials **146**(1–2): 20-29.

Matsushita, S., J. Yamashita, et al. (2006). "Effects of in ovo exposure to imazalil and atrazine on sexual differentiation in chick gonads." Poultry Science **85**(9): 1641-1647.

Moreno-Castilla, C. (2004). "Adsorption of organic molecules from aqueous solutions on carbon materials." Carbon **42**(1): 83-94.

Mozia, S., M. Tomaszewska, et al. (2005). "Studies on the effect of humic acids and phenol on adsorption–ultrafiltration process performance." Water Research **39**(2–3): 501-509.

Nadzialek, S., L. Spanò, et al. (2008). "High doses of atrazine do not disrupt activity and expression of aromatase in female gonads of juvenile goldfish (Carassius auratus L.)." Ecotoxicology **17**(6): 464-470.

Najm, I. N., V. L. Snoeyink, et al. (1991). "Effect of initial concentration of a SOC in natural water on its adsorption by activated carbon." Journal / American Water Works Association **83**(8): 57-63.

Newcombe, G., M. Drikas, et al. (1997). "Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol." Water Research **31**(5): 1065-1073.

Newcombe, G., J. Morrison, et al. (2002). "Simultaneous adsorption of MIB and NOM onto activated carbon: II. Competitive effects." Carbon **40**(12): 2147-2156.

Nghiem, L. D. and A. I. Schäfer (2002). "Adsorption and transport of trace contaminant estrone in NF/RO membranes." Environmental Engineering Science **19**(6): 441-451.

Ozaki, H., N. Ikejima, et al. (2008). Rejection of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) by low pressure reverse osmosis membranes. **58:** 73-81.

Papastergiou, A. and E. Papadopoulou-Mourkidou (2001). "Occurrence and spatial and temporal distribution of pesticide residues in groundwater of major corn-growing areas of Greece (1996-1997)." Environmental Science and Technology **35**(1): 63-69.

Pelekani, C. and V. L. Snoeyink (1999). "Competitive adsorption in natural water: role of activated carbon pore size." Water Research **33**(5): 1209-1219.

Pikaar, I., A. A. Koelmans, et al. (2006). "Sorption of organic compounds to activated carbons. Evaluation of isotherm models." Chemosphere **65**(11): 2343-2351.

Pirbazari, M., B. N. Badriyha, et al. (1992). "MF-PAC for treating waters contaminated with natural and synthetic organics." Journal / American Water Works Association **84**(12): 95-103.

Prasad, M. H. (1996). "REPRODUCTIVE EPIDEMIOLOGY IN SULFONAMIDE FACTORY WORKERS." Journal of Toxicology and Environmental Health **47**(2): 109-114.

Quinlivan, P. A., L. Li, et al. (2005). "Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter." Water Research **39**(8): 1663-1673.

Rietveld, L. C. (2005). Improving operation of drinking water treatment through modelling.

Rogers, H. R. (1996). "Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges." Science of The Total Environment **185**(1–3): 3-26.

Sass, J. B. and A. Colangelo (2006). "European Union bans atrazine, while the United States negotiates continued use." International Journal of Occupational and Environmental Health **12**(3): 260-267.

Schäfer, A. I., I. Akanyeti, et al. (2011). "Micropollutant sorption to membrane polymers: A review of mechanisms for estrogens." Advances in Colloid and Interface Science **164**(1–2): 100-117.

Schwarzenbach, R. P., B. I. Escher, et al. (2006). "The challenge of micropollutants in aquatic systems." Science **313**(5790): 1072-1077.

Shon, H. K., S. Vigneswaran, et al. (2004). "The effect of pretreatment to ultrafiltration of biologically treated sewage effluent: a detailed effluent organic matter (EfOM) characterization." Water Research **38**(7): 1933-1939.

Siripattanakul, S., W. Wirojanagud, et al. (2009). "Atrazine removal in agricultural infiltrate by bioaugmented polyvinyl alcohol immobilized and free Agrobacterium radiobacter J14a: A sand column study." Chemosphere **74**(2): 308-313.

Speth, T. F. (1991). "Evaluating capacities of GAC preloaded with natural water." Journal of Environmental Engineering **117**(1): 66-79.

Stoker, T. E., S. C. Laws, et al. (2000). "The effect of atrazine on puberty in male Wistar rats: An evaluation in the protocol for the assessment of pubertal development and thyroid function." Toxicological Sciences **58**(1): 50-59.

Summers, R. S., B. Haist, et al. (1989). "The influence of background organic matter on GAC adsorption." Journal of the American Water Works Association **81**(5): 66-74.

Swan, S. H., R. L. Kruse, et al. (2003). "Semen quality relation to biomarkers of pesticide exposure." Environmental Health Perspectives **111**(12): 1478-1484.

Thiruvenkatachari, R., W. G. Shim, et al. (2006). "A novel method of powdered activated carbon (PAC) pre-coated microfiltration (MF) hollow fiber hybrid membrane for domestic wastewater treatment." Colloids and Surfaces A: Physicochemical and Engineering Aspects **274**(1–3): 24-33.

Tyler, C. R., S. Jobling, et al. (1998). "Endocrine disruption in wildlife: A critical review of the evidence." Critical Reviews in Toxicology **28**(4): 319-361.

Van der Bruggen, B., J. Schaep, et al. (1999). "Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration." Journal of Membrane Science **156**(1): 29-41.

Van Maanen, J. M. S., M. A. J. De Vaan, et al. (2001). "Pesticides and nitrate in groundwater and rainwater in the Province of Limburg in the Netherlands." Environmental Monitoring and Assessment **72**(1): 95-114.

van Schagen, K., L. Rietveld, et al. (2008). "Control of the fluidised bed in the pellet softening process." Chemical Engineering Science **63**(5): 1390-1400.

Verliefde, A., E. Cornelissen, et al. (2007). "Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration." Environmental Pollution **146**(1): 281-289.

Villacañas, F., M. F. R. Pereira, et al. (2006). "Adsorption of simple aromatic compounds on activated carbons." Journal of Colloid and Interface Science **293**(1): 128-136.

von Gunten, U. (2003). "Ozonation of drinking water: Part I. Oxidation kinetics and product formation." Water Research **37**(7): 1443-1467.

Worm, G. I. M., A. W. C. van der Helm, et al. (2010). "Integration of models, data management, interfaces and training support in a drinking water treatment plant simulator." Environmental Modelling & Software **25**(5): 677-683.

Xia, S.-j., Y.-n. Liu, et al. (2007). "Drinking water production by ultrafiltration of Songhuajiang River with PAC adsorption." Journal of Environmental Sciences **19**(5): 536-539.

Xu, W., B. Gao, et al. (2011). "Influence of floc size and structure on membrane fouling in coagulation–ultrafiltration hybrid process—The role of Al13 species." Journal of Hazardous Materials **193**(0): 249-256.

Ye, M., H. Zhang, et al. (2006). "Study on the suitable thickness of a PAC-precoated dynamic membrane coupled with a bioreactor for municipal wastewater treatment." Desalination **194**(1–3): 108-120.

Yu, W.-Z., H.-J. Liu, et al. (2013). "Comparison of submerged coagulation and traditional coagulation on membrane fouling: Effect of active flocs." Desalination **309**(0): 11-17.

Zhang, Y., J. Tian, et al. (2011). "Effect of PAC addition on immersed ultrafiltration for the treatment of algal-rich water." Journal of Hazardous Materials **186**(2–3): 1415-1424.

Zheng, X., S. Plume, et al. (2012). "In-line coagulation prior to UF of treated domestic wastewater – foulants removal, fouling control and phosphorus removal." Journal of Membrane Science **403–404**(0): 129-139.

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