TRICLOSAN REMOVAL BY NANOFILTRATION FROM SURFACE WATER

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ABSTRACT

TRICLOSAN REMOVAL BY NANOFILTRATION FROM SURFACE WATER

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Nowadays, organic pollutants occurring in surface waters have raised substantial concern in public. Triclosan (TCS) is one of the antimicrobial agents which are utilized in both domestic and industrial application. In this study nanofiltration (NF) of TCS in surface water was investigated. Laboratory scale cross-flow device is operated in total recycle mode and DK-NF and DL-NF membranes were used. Kesikköprü Reservoir (Ankara) water was used as raw water. Effect of natural organic matter (NOM) content of raw water on TCS removal is searched through addition of humic acid (HA) into the raw water as to represent for NOM. Steady state permeate fluxes are monitored throughout the experiments to explore the flux behavior of the membranes. During the experiments, performance of the membranes is assessed by monitoring TCS, as well as other water quality parameters, such as UVA_{254} and total organic carbon (TOC) in the feed and permeates waters. Results obtained put forward that TCS removal by NF membrane is not as same as reported in the literature. In the literature, membrane removal efficiency is reported as above 90%. However, this study proved that this would be true if and only if one does not considers the adsorption of TCS by the system itself, in the absence of membrane. It is now clear that, because of adsorption of the TCS onto the experimental set up (feed tank, pipings etc.); the real TCS removal efficiency of the nanofiltration is around 60-70%.

Keywords: Membrane, Adsorption, Triclosan removal, Nanofiltration, Drinking water, adsorption onto labware.

ÖZ

NANOFİLTRASYON İLE YÜZEY SUYUNDA TRİKLOSAN GİDERİMİ

Öğütverici, Abdullah
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Organik kirleticilerin yüzey sularında bulunması toplumda artan endişe oluşturmaktadır. Triklosan (TCS) evsel ve endüstriyel alanda kullanılan antimikrobiyel bir madde ve bir çeşit organik kirleticidir. Bu çalışmada triklosanın yüzey sularından NF membran ile laboratuvar boyutta ters-akışlı cihaz kullanılarak tam çevrim modunda giderimi incelenmiştir. Çalışmada DL-NF ve DK-NF membranlar kullanılmıştır. Ayrıca araştırmada sularda bulunan doğal organik maddelerin TCS'nin membranla giderimi üzerindeki etkisi araştırılmıştır. Deneyler süresince çıkış akı değerleri ölçülerek membranın akı hareketleri gözlemlenmiştir. Deneylerde ham kaynak suyu olarak Kesikköprü Barajı (Ankara) suyu kulanılmıştır. Deneylerde TCS, UVA_{254}, toplam organik karbon (TOK) değerleri giriş ve çıkışta (permatta) ölçülerek değerlendirilmiştir. Sonuçlar literatürde %90 üzeri rapor edilen membran arıtımının gerçekte %60-70 seviyelerinde olduğunu göstermiştir. Bunun nedeninin triklosanın membranın kendisinden ziyade sistem besleme tankına ve boru çeperlerine yapışması olduğu gözlemlenmiştir.

Anahtar Kelimeler: Membran, Adsorplanma, Triklosan giderimi, Nanofiltrasyon, Yüzey suları, Laboratuvar malzemelerine adsorplanma.

To my family

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ABBREVIATIONS

CFV **:** Cross Flow Velocity

DDW **:** Distilled and Deionized Water

$\mathbf{J_{cwi}}$ **:** Clean water flux before raw water

$\mathbf{J_{rw}}$ **:** Raw water flux

$\mathbf{J_{cws}}$ **:** Clean water flux before cleaning

$\mathbf{J_{cwc}}$ **:** Clean water flux after cleaning

MF **:** Microfiltration

MWCO **:** Molecular Weight Cut-off

NF **:** Nanofiltration

NOM **:** Natural Organic Matter

ppm **:** Parts per million (mg/L)

ppb **:** Parts per billion (µg/L)

TMP **:** Transmembrane Pressure

TCS **:** Triclosan

HA **:** Humic Acid

CHAPTER 1

INTRODUCTION

Organic micropollutants have raised increasing concern in public and regulatory agencies because of their potential health effect on human and wild life. Triclosan is one of the main antimicrobial agents which are classified as organic micropollutant utilized in everyday life in different personal products such as hand soaps, cleaning liquids, toothpastes etc.

According to World Health Organization, development of Triclosan (chemical name 2.4.4'–trichloro-2'-hydroxydiphenyl ether) dates back to 1960s and concentration between 0.2% to 2% of triclosan effects as antimicrobial activity [1].

TCS is very widely used and produced chemical for example in Europe, around 350 tons of TCS produced and utilized annually [2]. And also in U.S. TCS is among the first seven most frequently utilized compound among 30 states and because of its widespread usage, in 139 of U.S. streams TCS is detected in 57.6% of them[3].

Excess utilization of these antimicrobial agents in everyday life result in occurrence of these chemicals in wastewater treatment plants (WWTP) effluent and so in surface water. As reported in the literature, after utilization of TCS, main route to environment is discharge of effluent from WWTPs and sludge, since TCS cannot be totally removed from the wastewater and because of its hydrophobic nature it deposits in solid phase[4].

Although triclosan has not been reported as toxic to mammals, it is reported that it has some toxic effect to aquatic life namely Dapnia manga, Pimephales promelas [5]. TCS is also classified as an endocrine disrupting chemical (EDC) and as a pharmaceutical and personal care product (PPCPs). In the removal of EDC/PPCPs from surface water, ultrafiltration, nanofiltration and reverse osmosis are selected removal methods in literature. Their low surface water concentrations of µg/L [6] makes nanofiltration, ultrafiltration and reverse osmosis necessary for TCS treatment.

Triclosan has a molecular weight of 290 [7]. Based on this molecular weight data according to Kimura et. al [8], nanofiltration and reverse osmosis membranes are preferred as effective in TCS treatment. Nghiem et. al. [9] indicated that membrane processes are necessary for high quality water production because of their high removal efficiencies of organic contaminants which are dissolved in water.

1.1. Objective and Scope

The main aim of this study is to determine the nanofiltration removal of Triclosan from Kesikköprü Reservoir water of Ankara. Different TCS concentration levels were selected in order to investigate concentration level effect on nanofiltration. Effect of different natural organic matter content level on nanofiltration was also another point to determine. Investigating the fouling behavior of NF membrane in existence of artificially spiked Humic Acid was also in the scope of this study.

CHAPTER 2

LITERATURE REVIEW

Antimicrobial agents that kill or inhibit the growth of microorganisms are utilized in many everyday household, personal care and consumer products. Because of their potential negative effect on human and animal life there is growing concerns about the emergence of these chemicals. Triclosan is one of the antimicrobial agents produced synthetically and used in pharmaceuticals and personal care products such as detergents, toothpastes, shampoos, deodorants, lotions, body washes, and dish washing liquids.

As reported by EPA, Triclosan (2.4.4’ –trichloro-2’-hydroxydiphenyl ether) is an antimicrobial agent which is chlorinated aromatic compound with functional groups including both phenols and ethers. Also reported that triclosan was first registered as a pesticide in 1969[10].

In literature, triclosan was classified as nontoxic to mammals in its natural form except at extremely high doses, however at low concentrations it is highly toxic to aquatic organisms namely plants and fish [5]. Also revealed in literature, triclosan blocks enzyme carrying proteins of aquatic organisms, and this result in bacterial resistance buildup [11]. Researchers have focused on treatment of triclosan from water and wastewater due to its molecular similarity to highly toxic chemical, namely dioxins [12]. Concerns on the use of Triclosan have increased not only due to its existence in wastewater treatment plan effluent but in human milks also [13].

2.1. Triclosan in water bodies

Trace organic contaminants are ubiquitous in treated secondary effluent and these effluents impact water bodies. Impacted water bodies contain these compounds in nanogram per liter level [3]. Triclosan is one of the organic micropollutants that exist in secondary wastewater effluent and in surface water in which secondary effluent was discharged.

Triclosan is persistent compound in environment due to its chlorinated structure [14] and volatilization is also negligible due low vapor pressure as 4*10-6mm mercury and a Henry’s law constant as 1.52*10-7 atm. m3/mol [19]. Hence, natural degradation of triclosan is not commonly encountered therefore some removal techniques should be applied in order to eliminate TCS from water.

2.2. Triclosan Removal Methods from Water

The advance treatment methodologies have started to be considered as efficient removal techniques in removal of antimicrobial agents due to deficiency of present wastewater treatment methods. Phototransformation, ozonation, sonolysis and nanofiltration are the techniques applied in TCS removal.

2.2.1. Phototransformation

Phototransformation processes seem to be one of the main elimination pathways of triclosan in the aquatic environment [15]. Several authors have studied the photochemical behavior of triclosan in different phases and mediums. Kanetoshi et al. conducted a photodegradation study of TCS on heterogeneous phase [16] and in thin mediums [17]. These studies confirmed TCS's photochemical degradation and formation of dichlorodibenzodioxin and trace amounts of trichlorodibenzodioxin. Ferrer et al. [18] revealed that the replacement of a chlorine atom by a hydroxyl group was the preferred degradation pathway. Considering the photodegradation behavior of triclosan, this compound is easily degraded by sunlight and UV light, both in the fiber coating and in aqueous media. Six photoproducts were detected in real wastewater and two of them, MCP (monochlorophenol) and DCP (dichlorophenol), were already initially detected in the sample. The other photoproducts were tentatively identified as dichlorohydroxydiphenyl ether, 2.8-DCDD, and a possible DCDD isomer or dichlorohydroxydibenzofuran. Therefore, the photodegradation of triclosan is a subject of special concern due to the generation of highly toxic photoproducts.

Photolysis of triclosan mentioned as effective removal mechanism especially pH 8 and above [19]. However, in this study, pH of the feed water varies between pH 6 and 7 in which most Triclosan (pKa 8.1) is in its photostable form. Therefore, losses due to photolysis could be considered as negligible.

2.2.2. Ozonation

Ozonation is studied as another advance treatment method for the removal of antimicrobial agent from water. Suarez's [20] research shows that, the feasibility of wastewater ozonation as a means of oxidizing and deactivating triclosan was qualitatively evaluated by monitoring depletion of 0.5 μM triclosan from samples of pilot-scale and full-scale wastewaters dosed with various O3 concentrations(i.e., 8:3*10-5 mol/L to 1:3*10-4 mol/L). Triclosan transformation reactions occurred too rapidly during ozonation of wastewaters.

Triclosan removal efficiencies were evaluated by applying varying O3 doses. Second-order reaction rate constants were figure out for the TCS reaction with O3. The antibacterial activity of the triclosan molecule is efficiently eliminated by reaction with O3 [21].

Ozonation seems to be an effective technique for increasing the removal efficiency of triclosan after biological treatment, with the objective of minimizing its discharge into receiving waters. Oxidation of TCS was governed mainly by direct reaction with O3, leading to rapid, efficient elimination of the triclosan molecule's antibacterial activity, during municipal wastewater ozonation [20].

2.2.3. Sonolysis

Sonolysis is defined as mechanical and chemical strong digestion of chemical reagents in the liquid phase [22].The research of Sanchez et al. [23] revealed that sonolysis of triclosan could be another removal method for micropollutants from aqueous medium. It is reported that the presence of matrix components (e.g. salt, natural organic and particulate matter) may dramatically change the efficiency of sonochemical oxidation processes during TCS removal in membrane treatment.

Degradation rate of TCS is evidently affected by the matrix components present in the water samples. The effect of matrix compound could be as increase or decrease according to matrix compound’s property. It was reported that degradation order was the highest in seawater and very less in wastewater influent. [23]

2.2.4. Membrane Filtration

Advanced treatment technologies are necessary for high quality potable drinking water not only for human beings but also for other living organisms’ consumption. Membrane technology has become widespread advanced treatment technology applied in treatment of water and wastewater and resulting in high quality of water from all kind water sources.

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and RO membrane processes are applied high tech membrane treatment processes in water and wastewater treatment. Although MF and UF mentioned here, many application was encountered in literature for TCS removal from water. Many treatment plants are preferring NF instead of RO due to low power utilization [24].

Osmosis is defined as transport of water through a selective membrane to decrease concentration difference between the solution separated by the membrane [25]. Reverse osmosis is the reversal of this process in which solution is pressurized through semi-permeable membrane and solute concentrate enriched. During reverse osmosis process, solute diffuse through semi permeable membrane in slower way and concentration of the solute on the other side of the membrane is going to be less than pressurized side. By this way compounds desired to be removed from the water could not diffuse or less diffuse to the other side and removal of undesired compound is going to be accomplished by this way.

Main impediments during RO process are production of the semi permeable membrane and high pressure requirement for RO application [26]. Commercially available membranes are thought to be semi permeable however it was mentioned in literature that these membranes are not produced truly semi permeable and utilize membrane and solute interaction and some additional diffusion limitation to increase removal efficiency [27, 28].Hence, it was reported that none of the commercially available RO membrane can fully reject dissolved compound and partially treat low molecular weight and small neutral compounds [28, 29]. Contrary to common belief, researchers reported that membrane with smaller pore size not always reject higher than membrane with larger pore size in particular for low molecular weight neutral organic compounds[30]. Thus rejection mechanism of RO is described by two main mechanisms as limiting compound diffusion through membrane and sterically or chemically preventing the passage across the pores [31].

Nanofiltration of Triclosan

Membrane treatment processes are becoming an indispensible part of high quality water production. High dissolved contaminant removal efficiency of these treatment procedures has led to widespread utilization of these techniques [9]. Nanofiltration (NF), in particular, has been increasingly considered as a reliable and affordable technique for the production of high quality water from unconventional sources such as brackish water, polluted surface water, and secondary treated effluent where micropollutants are to be removed [32, 33]

During nanofiltration of trace organic contaminants from water, different interactions occur between membrane and compounds to be removed. During rejection of these contaminants complex interaction of electrostatic repulsion, steric hindrance solution and solute properties take place [34].

It was reported that size exclusion, electrostatic repulsion, and adsorption are three main rejection mechanisms for nanofiltration of organic pollutants including TCS. Transport of organic solute during nanofiltration can be accomplished by convection and diffusion [35, 36]. However, the main rejection for the organic compounds is size exclusion during steady state operation of nanofiltration [37].

Size exclusion is one of the basic mechanisms during nanofiltration in which compounds larger than membrane MWCO captured by the membrane. Other rejection mechanisms are quite complex, namely electrostatic exclusion and hydrophobic-hydrophilic interactions between membrane and compounds to be removed [34].

Another prevailing mechanism is the Donnan equilibrium in which interaction occurs between surface of charged membrane and ions present in the solution. [38]. In literature it was mentioned that Donnan equilibrium is dependent not only on membrane chemistry, surface charge and feed water composition but also flux and hydrodynamic conditions [39, 40]. Ion adsorption to membrane surface is related to membrane charge density which is dependent on ionic strength and concentration [41].

Another factors effecting rejection mechanism of membrane filtration of TCS from water are: feed water type, characteristics of solute and type of membrane [42, 43, 44].

In addition to that, rejections of organic compounds with nanofiltration are correlated with molecular width and compound hydrophobicity [45, 46]. Triclosan shape was determined with a computer program and found out to be cylindrical shape compound in its lowest energy state with a molecular width of 0.693 nm and for tight and loose NF membranes utilized with pore size with 0.68 and 0.84 nm, respectively; hence it was reported that size exclusion becomes the major rejection mechanisms of TCS during nanofiltration [54]. Similar observation was also mentioned by Chang [53] and reported that main rejection mechanism of size exclusion did not changed even after fouling.

Adsorption of hydrophobic compounds onto the surface of nanofiltration and reverse osmosis membrane are also determined by some researchers. Even at very low concentration this adsorption was observed (100 ppb)[8]. This adsorption could be thought as removal mechanism however capacity of the membrane is finite.

Another point to mention is continual decrease in the feed solution during nanofiltration and reverse osmosis processes. This phenomenon was observed in most of the studies and this decrease was attributed to adsorption of TCS to the membrane surface [8, 54]. As can be depicted from Figure 1 [47], feed water TCS concentration of the treatment system was decreased in all three kind of membrane tested, namely NF-270 NF90 and BW-30. This decrease was attributed, by the researchers, to the adsorption of TCS on membrane itself. In order to prepare realistic nanofiltration set-up it was suggested that this adsorption effect should be taken into account and membrane should be saturated with target compound [8].

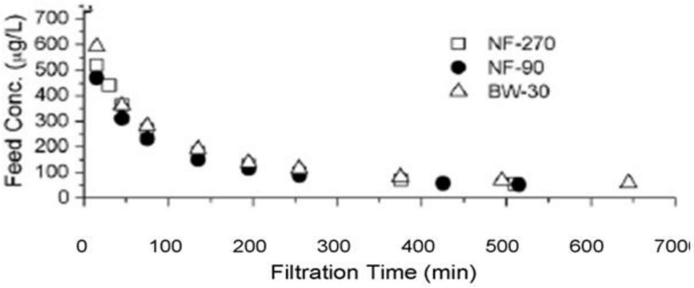

Figure 1 Feed water TCS concentration decrease (Nghiem's study) [47]

2.2.4.1. Membrane Fouling

Fouling of membrane is defined as the reduction in water transport per unit area of membrane (flux), caused by substances in the feedwater that accumulate either on or in the membrane. [48]. Fouling can be attributed to concentration polarization, adsorption, gel layer formation and pore plugging.

Gradual increase in the retained solutes at the membrane surface causes a diffusive flow back to the feed part, and then a concentration profile is formed in the boundary layer at steady-state conditions. This phenomenon is called concentration polarization [49]. Concentration polarization occurs due to osmotic pressure raise, increase of resistance to permeation and fouling susceptibility [50].

Solute molecules on and in the membrane result in resistance and this phenomenon is called as adsorption.

Pore plugging is defined as entrance of bulk phase particles which are small enough to the membrane pores deposition on their surface [51]

Both of concentration polarization and membrane fouling affects the efficiency of the separation process.

Fouling layer on the membrane surface alter the rejection characteristic of the membrane with its surface charge and hydrophobicity, hence its rejection efficiency during treatment [3]. Not only increase in the rejection was observed but also decrease was evident in the rejection of the trace organic contaminants during nanofiltration including triclosan [54]. In another study, with different kind of organic contaminants, including hydrophilic, hydrophobic, non-ionic, both increasing and decreasing rejections trends were observed [3].

Foulant characteristics are also important factor on the rejection mechanisms. Different studies employed different kind of foulants in their experiments. Alginate, Humic Acid, Bovine serum albumin, and colloidal serum are some of them and these foulants were significantly larger than the pore size of the membrane employed in the Nghiem's study [54]. Main aim was to complete rejection of these compounds and formation of the fouling layer. Foulant concentration ranging from 0 to 40 mg/L was also studied and resulted in increasing membrane fouling up to 20 mg/L humic acid and further fouling was not investigated above 20 mg/L[54].

Compound physicochemical characteristic also affect the rejection of triclosan in nanofiltration. Strong adsorption affinity of TCS showed low retention trend in NF-90 and NF-270 membranes however addition of humic acid as a prefoulant to the membrane these rejection values improved. [54]

Triclosan at typical environmental pH levels (i.e. 6 to 8) would be observed in both ionized and neutral state and even in ionized state triclosan stays hydrophobic nature.

Saturation of membrane with solute to be filtrated is also mentioned in the literature [52]. Without saturation of the membrane evaluation is not possible.

Rejection of triclosan studied in fouled NF membranes with humic acid resulted in higher rejection than fouled NF membranes with humic acid/Ca+2. This was mainly due to becoming of the NF membrane more hydrophilic characteristic after fouling with humic acid/Ca+2 [53].

It was reported that effect of fouling as a result of blocked pores on the membrane solute rejection was increased for loose membranes [53].

CHAPTER 3

MATERIALS AND METHODS

3.1. Source Water

During TCS removal experiments, Kesikköprü Reservoir water was used as raw water source. The collected raw water samples from the lake were subjected to temperature and pH measurement and were immediately shipped to the laboratory and kept at +4 0C and dark prior to experiments. Raw water sample were analyzed in terms of TOC, TCS and UVA254. Characteristics of Kesikköprü Reservoir water samples collected at different months between in the years 2010 and 2012 are tabulated in Table 1.

Table 1 Characteristic of Raw water (Kesikköprü) Samples Taken During the Study

	Temperature (^{o}C)	pH	TDS (mg/L)	Coliform (/100 mL)	TOC (ppm)	TCS (ppt)
2010 January	5.9	8.52	885	53	1.08	
2010 February	7.1	8.12	877	40	5.51	
2010 March	11.4	8.67	855	17	6.15	
2010 May	21.6	8.39	831	Too much to count	3.73	2.37
2010 July	23.5	8.29	826	Too much to count	4.65	8.21
2010 September						16.47
2010 October						2.03
2010 November						5.00
2011 January						2.92
2012 March					2.68	

3.2. Compound of Concern-TCS

Characteristic of TCS are given in Table 2. In this table molecular weight and some other properties are shown. Together with this, triclosan is reported as very hydrophobic compound even in an ionized stage [47].

Table 2 Characteristic of Triclosan [54]

MW (g/mol)	pKa	Charge at pH 8	Log Dow	Molecular dimension (nm)	
289.6	8.14	Neutral	4.70	0.693	1.419

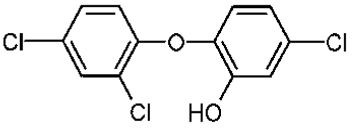

Figure 2 Chemical Structure of TCS [54]

3.3. Membrane Filtration Set-Up

In all set of experiments, lab scale cross flow membrane filtration system (GE Water, Osmonics, SEPA® CF II) was used. Rectangular flat sheet membranes were used in this study set-up and effective area of 140 cm2 with dimensions of 19 cm and 14 cm.

The membrane filtration system is composed a 35 liter feed tank, high pressure pump (1.1 kW), a cell body unit for membrane placement and a control panel for frequency adjustment, cell holder pressure gauge, concentrate pressure gauge. The cell body, concentrate flow control valve and concentrate pressure gauge are made of 316 stainless steel (SS316). In addition to these main components there are several connections and tubing etc. made of stainless steel or nylon-seal (Dayco- Imperial) plastic. Schematic representation of the system is shown in Figure 3.

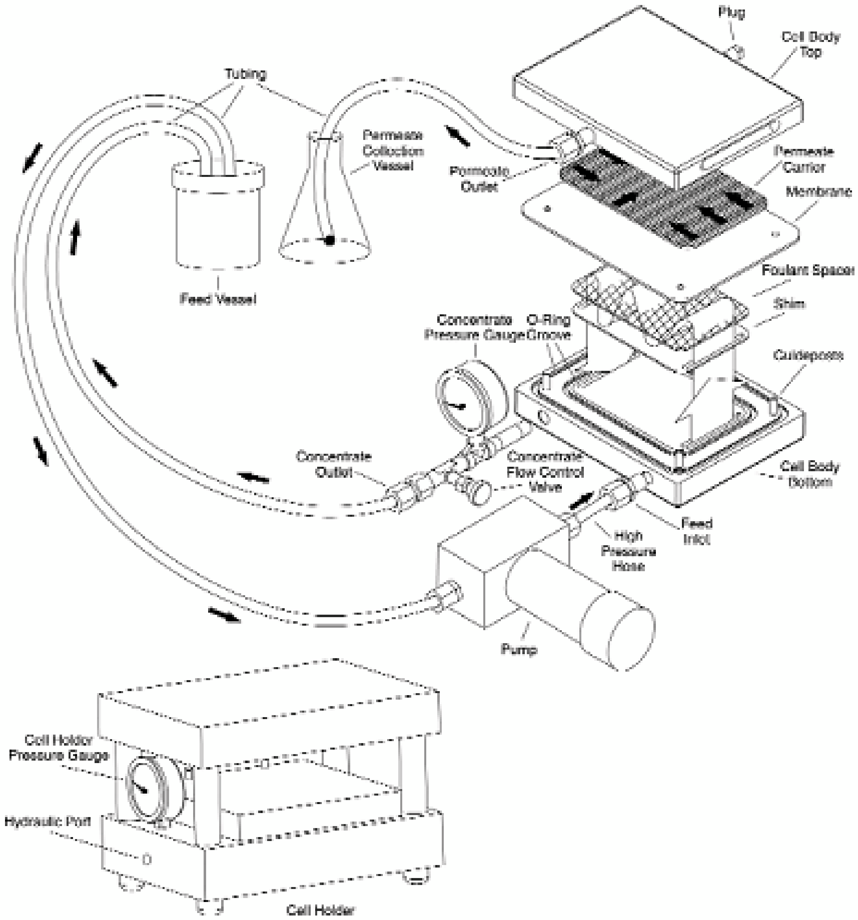

Figure 3 Schematic representation of lab-scale membrane filtration set-up[55]

By adjusting concentrate flow control valve, pressure in the membrane cell was adjusted to required level. The required pressure in the membrane cell is produced by the pump in the system. Water in the feed tank is pressurized and sent to the feed inlet and introduced to the membrane. By cross flow motion, the feed water hits onto the membrane surface and because of membrane semi-permeable characteristics, some portion of the water goes to permeate and other portion goes to concentrated outlet. In permeate flow, concentration of the compound that we want to remove from water decreases. In all set of the experiments total recycle mode is applied in which permeate and concentrated flow are recirculated back to feed tank.

Feed water temperature in the feed tank is kept at 19±2 ^{0}C by water jacket around the feed tank by continuously feeding tap water to this jacket.

Flux measurements were accomplished by measuring the time needed for a 0.05 L of permeate collection from the permeate flow line. This time was recorded and in order to convert this data to flux value, amount of collected water (0.050 L) was divided by the multiplication of area of the membrane and the recorded time needed for 0.05 L of permeate collection. Finally flux value with a unit of L/m2.h was obtained.

Frequency of flux measurements was conducted hourly, in general, to see whether system reached to steady state or not. Observing the same flux value for two or more hours indicated that system reached to stable condition and this data was taken as steady state flux value for that stage of the experiment set.

3.4. Pretreatment of Raw Water

Kesikköprü Reservoir water was pretreated before the experiments to remove particles which may harm the membranes. Microfiltration is applied to this water under vacuum. A 2.5 μm ashless cellulose filter paper (Whatman 42) is used for this microfiltration.

3.5. Nanofiltration

In this study, two different thin-film composite nanofiltration membranes, namely DL-NF, DK-NF were tested. Characteristics of the membranes utilized during the experiments are shown in Table 3.

Table 3 Characteristics of the membranes utilized in this study

Membrane Name	Polymer Structure	pH Range	Rejection Size	Typical Flux/psi GFD@PSI
DL-NF	Thin Film	2-11	96% $MgSO_4$	31/100
DK-NF	Thin Film	2-11	98% $MgSO_4$	22/100

There exist two different operation modes for experimental set-up namely total recycle mode and concentrate mode. In total recycle mode, permeate and concentrated outlet are redirected to the feed tank, however in concentrated mode just concentrated outlet is redirected to the feed tank. In this study only total recycle mode was applied. Schematic representation of total recycle mode is shown in Figure 4

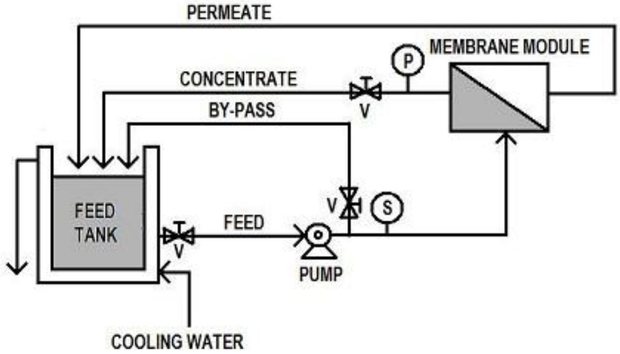

Figure 4 Total recycle mode operation of filtration set-up (V: Valve, P: Pressure Gauge & S: Suction Gauge)

Water jacket around the feed tank helps to keep the temperature of the feed water at 19±2 ^{0}C. This water jacket was filled with tap water and tap water was kept open during experiments. Filtration time changes between 8 to 56 hours in different sets of experiments because of the time requirement for the membrane set-up to reach steady-state condition.

In all set of experiments, cross flow velocity was set to 1.2 m/s and pressure to 6.9 bar. In order to check the system steady state condition, permeate flux was measured, and observing a constant permeate flux in at least three consecutive measurements was taken as an indication of steady state condition. After reaching the steady state, samples were taken from the permeate and subjected to the analysis.

Nanofiltration experiments were conducted in overall 7 sets of experiments. In all of the sets, feed water was spiked with TCS owing to the fact that TCS in the raw water was very low (varying between 2-16 ppt, as shown in Table 1) to allow for the detection of TCS in the effluent, and hence to determine the TCS removal performance of the system. In the first set of experiments (i.e. experiment Set 1), DL-NF membrane was employed at 6.9 bar TMP and 1.2 m/s crossflow velocity (CFV) with the feed water spiked with 500 ppb TCS. In experiment Set 1, adsorption behavior of TCS onto the inner surfaces of the installation tubes and feed tank was evident. So, it was decided to explore this behavior before proceeding thru the nanofiltration experiments. Accordingly, experiment Sets 2 and 3 are the sets designed toward this issue and therefore, will be called as "adsorption" part of the study. In these sets, membrane was removed from its holder in the filtration set-up and feed water was allowed to circulate within the system in the absence of membrane. In other words, these sets of experiment were conducted without membrane in order to investigate system adsorptive behavior. Two different TCS concentrations, namely, 750 and 1250 ppb, were employed. Due to not having a membrane in the filtration set up, pressure and CFV parameters were not applicable for the Set 2 and 3.

The remaining four sets (Set 4-7) of experiments were conducted with DK-NF membrane at 6.9 bars and 1.2 m/s CFV. In Set 4 and 5, the same uncompacted membrane was utilized whereas in Set 6 and 7, new membrane was used following its compaction. During the experimental sets from 5 through 7, humic acid was also spiked to the feed water, as a source of natural organic matter (NOM), in order to determine the performance of nanofiltration at different level of NOM. 10 mg/L humic acid (as TOC) was spiked to feed water for Set 5 and 6, and this amount was set to 26 mg/L in Set 7. This humic acid spiking level was determined according to natural TOC level of

Kesikköprü Reservoir water (avg 5 mg/L) shown in Table 1. TCS concentration was 2500 ppb in Set 5 whereas it was set to 5000 ppb in Set 4, 6 and 7.

HA was preferred as a model NOM, since NOM in natural surface water consists of about 70% of HA[56]. Humic acid was spiked into feed tank as soon as membrane placed into its holder for Set 5. However, stabilization of TCS concentration was not accomplished at that stage and it was decided to spike humic into the feed tank after a stable TCS concentration was accomplished, for Set 6 and Set 7. Operational conditions applied during all these studies are summarized in Table 4.

Table 4 Experimental Matrix

Set	**Membrane**	**Pressure (bar)**	**Cross Flow Velocity (m/s)**	**Initial TCS Concentration (C_0) (ppb)**	**Humic Acid Addition (as mg/L TOC)**
Set 1	DL-NF	6.9	1.2	500	-
Set 2	No membrane	Not Applicable	Not Applicable	750	-
Set 3	No membrane	Not Applicable	Not Applicable	1250	-
Set 4	DK-NF	6.9	1.2	5000	-
Set 5	DK-NF	6.9	1.2	2500	10
Set 6	DK-NF	6.9	1.2	5000	10
Set 7	DK-NF	6.9	1.2	5000	26

During the nanofiltration test runs, once steady state condition was reached, permeate samples were collected and analyzed for their TCS content, UVA254 and pH levels.

3.5.1. Operational Strategy for Preparation of Filtration Set-Up and Membrane for Experiment Sets 4-7

Before experiments, system was cleaned with methanol in order to remove all the TCS residues remaining in the system from previous operation(s) (if present). After cleaning phase, membrane was placed into its holder and the system was operated with clean water until steady state was reached. Followingly, feed tank was emptied and membrane was removed from the system. Then, feed tank was refilled with the raw water which was spiked with desired concentration of TCS. System was let to stabilize and reach to stable TCS concentration. After reaching stable TCS concentration membrane was placed into its holder in system and TCS concentration at that time was taken as initial TCS concentration in treatment calculation.

3.5.2. Cleaning and Preparation of Membranes

During all experimental sets, membrane filtration protocol was applied in which there are seven steps to follow as shown in Table 5. These steps are also presented in Figure 5 in the form of flow diagram followed in a single run process. Table 5 provides the detail of operational conditions maintained during each step. As seen from Table 5and Figure 5 firstly, compaction step is applied. In this step, the membrane is compacted with a pressure (13.8 bar) higher than the normal operating pressure (6.9 bar), so that the swelling or compaction of the membrane in the further steps is minimized. The compaction duration is 24 hours. This part of the experiment is optional and not applied in all sets. Compaction is applied if swelling in membrane was experienced in previous experimental set. Then, in second step, membrane cleaning is accomplished by operating the system with acidic solution at pH 3 and then, with alkaline solution at pH 9. Between acidic and alkaline solution phases, DDW (distilled and deionized water) is fed to feed tank, so solution pH change would not harm the membrane. During membrane cleaning phase pressure is lowered to 3.5 bars. In the third step, clean water is applied then the system In this step, system feed tank is filled with distilled and deionized water (DDW). Membrane filtration system is operated until stable flux values are observed and flux values are recorded with respect to time. After completing clean water step, system feed tank is filled with raw water (Step 4), Kesikköprü Reservoir water. TCS spiking to the feed tank also is implemented at this step. Consecutively, system feed tank is filled with DDW and the same procedure is applied as in clean water step. Chemical cleaning process is conducted and again clean water (DDW) step is applied and flux values are recorded

In each step mentioned above, time course variation of flux values are monitored and steady state values are recorded. Each step is treated separately during these assessments. Therefore, the time scale presented in tables and figures throughout the thesis starts from zero.

Table 5 Nanofiltration Experiment Steps Applied

	Pressure (Bar)	Feed Water	Cross Flow Velocity (m/s)	Duration
Phase1:Compaction (optional)	13.8	DDW*	1.2	24 hours
Phase 2:Cleaning of Membrane	3.5	HNO_3 @ pH 3	0.5	1 hour
	3.5	DDW	0.5	1 hour
	3.5	NaOH @ pH 9	0.5	1 hour
	3.5	DDW	0.5	1 hour
Phase 3:Clean Water Flux Before Raw Water	6.9	DDW	1.2	Until steady- state is reached
Phase 4:Raw Water Flux	6.9	Raw Water (Microfiltrated)	1.2	Until steady- state is reached
Phase 5:Clean Water Flux Before Cleaning	6.9	DDW	1.2	Until steady- state is reached
Phase 6:Cleaning of Membrane	3.5	HNO3 @ pH 3	0.5	1 hour
	3.5	DDW	0.5	1 hour
	3.5	NaOH @ pH 9	0.5	1 hour
	3.5	DDW	0.5	1 hour
Phase 7:Clean Water Flux After Cleaning of the Membrane	6.9	DDW	1.2	Until steady- state is reached

*DDW-distilled and deionized water

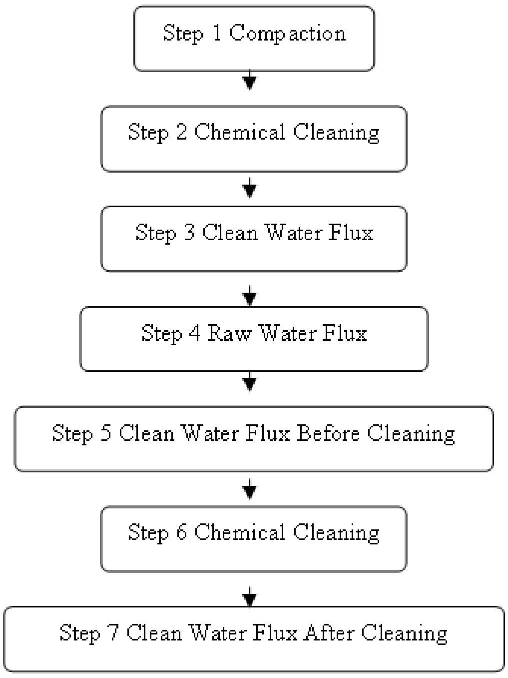

Figure 5 Single Run process for TCS Nanofiltration

3.5.3. Evaluation of Filtration Performance by Flux Measurements

Membrane filtration was primarily evaluated by flux measurements. Following flux values were determined: clean water flux before raw water (Jcwi): is the flux determined with the clean or virgin membrane, raw water flux (Jrw): is the flux determined with Kesikköprü water. While clean water flux before cleaning (Jcws) is the clean water flux before chemical cleaning is applied and clean water flux after cleaning (Jcwc) is again the clean water flux after chemical cleaning.

Reversible and/or irreversible accumulation of the filtrate increases with time on the surface of the membrane is natural consequence of the filtration and result in flux decline. Difference between clean water flux before raw water (Jcwi) and raw water flux (Jrw) gives the flux decline on the membrane. Concentration polarization and fouling are the two phenomena result in decline in the flux. Concentration polarization is totally reversible process that while fouling can either be reversible or irreversible depending on the cause for it, such as precipitation, adsorption, cake formation and. pore blocking. If the reduced flux could be restored by cleaning this is called as reversible fouling and vice versa.

On the other hand, flux recovery is calculated by the division of clean water flux before raw water (Jcwi) by clean water flux before cleaning (Jcws). In order to calculate flux decline due to concentration polarization percentage difference of Jcws and Jrw data were utilized. Similarly, during flux decline due to fouling calculation Jcwi and Jcws data were utilized. Calculation method is given in Table 6.

Table 6 Calculation equations of flux decline and flux recovery

Definition	Calculation
Flux Decline	[[(Jcwi)- (Jrw)]/(Jcwi)]*100
Flux Recovery	[(Jcws)/ (Jcwi)]*100
Flux Decline due to concentration polarization	[[(Jcws)–(Jrw)]/ (Jcws)]*100
Flux Decline due to Fouling	[[(Jcwi)- (Jcws)]/ (Jcwi)]*100

Difference between the value of clean water flux before cleaning and clean water flux after cleaning gives whether fouling occurred or not.

3.6. TCS Adsorption onto Teflon

In order to investigate the adsorption behavior of TCS onto the material other than plastic (of the experimental set up), adsorption experiments were conducted in Teflon made containers.

For the teflon adsorption experiment set, teflon crucible (5 cm in diameter and 7.5 cm height) (total inner area 0.0137 m2 total volume: 0.000147 m3 =147 mL.) was used. This crucible, including raw water spiked with desired TCS concentration (i.e., 1250 ppb), was kept at 19±2 °C. And hourly samples were taken and TCS concentration was monitored. In order to see the effect of temperature on the adsorption, the same experiment was repeated at +4 °C.

3.7. Analytical Methods

3.7.1. UV Spectroscopy Analysis

Varian 100 Spectrophotometer was used in ultraviolet absorbance (UVA) measurements. This spectrometer was connected a computer and 1-cm quartz cells was employed. In order to decrease interferences from compounds such as nitrate, nitrite, ferrous iron and bromide (APHA, AWWA, WEF, 1998) wavelength of 254 was selected. Device was calibrated with DDW.

3.7.2. Triclosan Measurement

LC/MSMS (Agilent 6410 Triple Quad) and HPLC (Shimatzu LC- 10AT VP) devices were, occasionally, used for the measurement of TCS. TCS concentrations of samples were measured via High Performance Liquid Chromatography (HPLC) (Shimadzu, LC-10AT vp). Nucleosil C 18 (4.6 mm*250 mm) column was employed. Device was equipped with SPD-10A VP Shimatzu UV-Vis detector set at 280 nm and retention time was adjusted to 6 minutes. Acetonitril (75%) and ultra pure water (25%) was utilized at a flow rate of 1.5 ml/min with an injection volume of 20 μL.

LC/MSMS (Agilent 6410 Triple Quad) was also employed in this study. Methanol (75%) and ultra pure water (25%) was utilized as solvent with a flow rate of 0.5-1 ml/min with an injection volume of 20 μL. Nucleosil C18 column also utilized in this device.

3.7.3. Total Dissolved Solids

Total dissolved solids (TDS) and conductivity of the samples were measured directly by using a Hach Sension 378 conductivity meter.

3.7.4. pH

Measurement of pH of the samples was conducted by Hach Sension 378. The device was calibrated by calibration solutions supplied by the producer of the device.

3.7.5. Temperature

The Hach Sension 378 device can also measure temperature with its embedded temperature sensor so temperature was measured by using the same device.

3.7.6. Total Organic Carbon (TOC)

In order to analysis samples in terms of Total Organic Carbon contents TOC-5000A model TOC analyzer (Shimadzu, Japan) device was utilized. This device applies high temperature combustion method (APHA, AWWA, WEF, 1998). Carrier gas of the device was high purity oxygen and this gas used as also for sparging purposes. Because main aim is to measure organic carbon amount in the samples inorganic carbon should be removed. To ensure that inorganic carbon is totally removed from the sample dry air is sent to samples during 10 minutes and samples were sparged with this dry air. pH adjustment were done by using 0.05N HCl. This acid was used in order to remove inorganic carbon from the samples through stripping via dry air sparging. pH range of samples and standards change between 2.5 and 3 for effective measurement of TOC. Injection number of the samples determined automatically by the device according to standard deviation and ranged between 3 and 5 times.

3.7.7. Humic Acid (HA)

HA measurements were accomplished via TOC measurements. However, TOC values could not be measured using TOC analyzer in the presence of TCS in water owing to the fact that TCS is prepared in methanol which contributes to TOC, causing mismeasurements of TOC. Therefore, UVA254 was considered as a surrogate parameter for TOC measurement.

HA solutions were prepared with concentrations of 7.9, 4.8, 3.5, 2.3 mg/L TOC and their UVA254 levels were measured. And correlation between TOC and UVA254 was established and measurement was done accordingly. Compiled data is given in appendix Table A-23

CHAPTER 4

RESULTS

In this study, performance of DL-NF and DK-NF (GE/Osmonics) nanofiltration membranes were tested for the removal of different concentration of spiked TCS (triclosan) from the Kesikköprü raw water source. Prior to all experimental sets raw water was microfiltrated to remove particle which could harm the membrane, if present.

Main objective of the study was to investigate the removal of TCS from water source by nanofiltration and to explore the effect of natural organic matter content of the source water on the TCS removal performance of the nanofiltration process.

3.8. TCS Removal by DL-NF Membrane (Set 1)

In this set of the study, DL-NF membrane was utilized. System feed tank was filled with the Kesikköprü Reservoir water sample as raw water and TCS was spiked to the feed tank at 500 ppb (microgram/liter). Membrane was not compressed for this experiment. Pressure during this experiment was kept at 6.9 bars and 1.2 m/sec cross-flow velocity. The temperature of the feed water was 19±2 ^{0}C

This set of experiment was conducted for 57 hours of raw water filtration in order to get stable flux value. The flux value attained at steady state was 38.7 L/m^2.h.

Flux values are presented in Figure 6. As seen from this figure, steady-state flux values for this set were 46.1 L/m2.h, 38.7 L/m2.h, 45.9 L/m2.h, 49.5 L/m2.h for clean water flux before raw water (Jcwi), raw water flux (Jrw), clean water flux before cleaning (Jcws), clean water flux after cleaning (Jcwc), respectively.

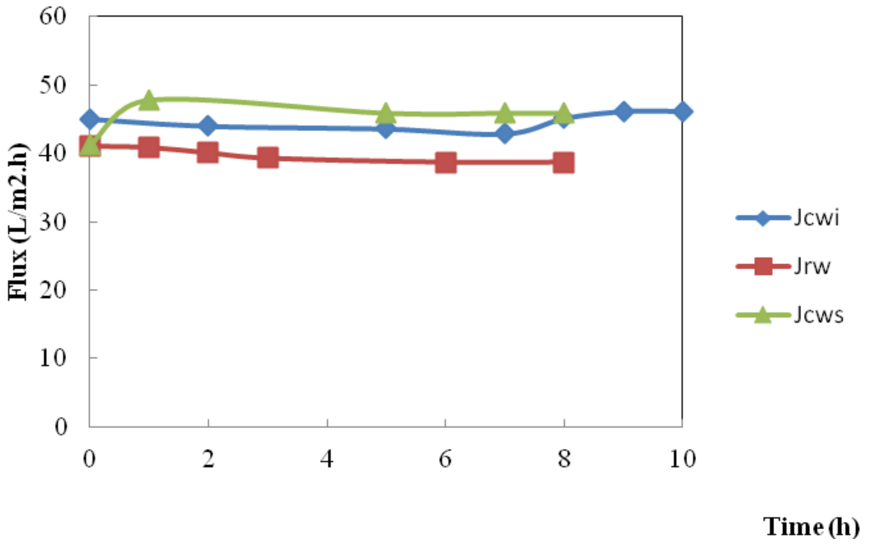

Figure 6 Flux values for DL-NF membrane (Set 1) (TMP: 6.9 bar; CFV: 1.2 m/s, TCS C0: 500 ppb)

On the other hand, for TCS concentrations, actually, it was expected to have stabilized feed water concentration since system was operated in a total recycle mode in which permeate and concentrate streams were returned back to feed tank. So, characteristic of feed water was expected to not change much. However, during the experiment, TCS concentration in feed water decreased from 512 ppb to 175.7 ppb. This result led to suspicion about the real treatment efficiency of the membrane system. Because, TCS removal efficiency appeared to be 57.1% when one considers influent TCS concentration measured as 175.7 ppb at time T8, as seen from Table 7, whereas it would be calculated as 85.3% when one considers the originally spiked TCS concentration at the beginning of the experiment (i.e. 512.7 ppb at time T0). So, this point should be cautiously taken into consideration in order not to report an overestimated removal efficiency which could mislead the readers. TCS removal efficiency during experiment is given in Figure 7.

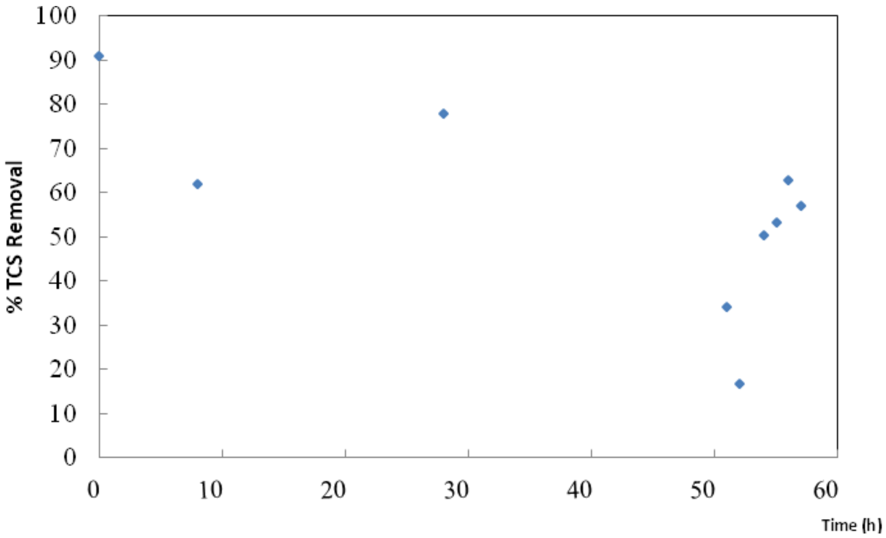

Figure 7 TCS Removal Percentage with DL-NF Membrane

Table 7 TCS Removal with DL-NF Membrane (TMP=6.9 Bar; CFV=1.2m/s)

	Time (h)	TCS (ppb) (influent)	TCS (ppb) (effluent)	TCS Removal (%)
T0	0	512.7	45.8	91.1
T1	8	207.3	79.1	61.9
T2	28	158.2	35.0	77.9
T3	51	117.4	77.2	34.2
T4	52	102.0	85.0	16.7
T5	54	165.3	82.1	50.3
T6	55	168.9	78.9	53.3
T7	56	207.3	77.3	62.7
T8	57	175.7	75.5	57.1

In fact, at first look, such decrease in the feed TCS concentration can be attributed to the adsorption of TCS onto the membrane itself, so that TCS was retained on the surface of membrane and in a way, was not returned to the feed tank via concentrate stream during the total recycle mode of operation. In the study of Nghiem et. al. [47] continual decrease in the feed concentration was attributed to adsorption of triclosan to the membrane surface. In other words, TCS removal mechanism was mainly an adsorption to the membrane surface with irreversible fouling. On the other hand, if it had occurred in our case, it would be expected to experience a membrane clogging problem which would be reflected in the flux data (Figure 6). However, as can be seen from these flux data, such a clogging problem was not evident, at least to the expected extent. Therefore, attempts were directed toward the understanding of the real cause for observing such a drastic decrease in the feed TCS concentration with time. i.e. whether adsorption of TCS onto the membrane surface itself or adsorption onto the inner surfaces of the feed tank and/or installation tubes of the system takes place. To that purpose, the membrane was removed from the filter holder and the system was operated in the absence of the membrane as described below.

Although flux values shows stable trend, due to fluctuations in the percentage removal of TCS during nanofiltration with DL-NF membrane, another membrane, namely DK-NF membrane was utilized for the rest of the study.

3.9. TCS Removal by the filtration set-up alone in the Absence of Membrane (Set 2 and Set 3)

As stated above, membrane was removed from the system and feed tank was filled with 5 liters of Kesikköprü raw water and TCS was spiked to the feed tank at two different concentrations (i.e., 750 ppb and 1250 ppb). System was operated for 120 hours.

During these experiments, due to not having membrane in the system, operational parameters of pressure difference and cross flow velocity were not applicable; however temperature was kept at 19±2 ^{0}C.

In order to assess the behavior of TCS within the filtration set-up only, two sets of experiment (Set 2 and Set 3) were designed as also indicated in Table 4. Both experiments were the same except their initially spiked TCS concentrations. In the former experiment, spiked TCS concentration was 750 ppb whereas in the latter one it was 1250 ppb. After each set, system is washed with methanol so that remaining residual TCS in the system was removed.

Table 8 and Table 9 present the time course variation of the TCS concentration in the feed tank. Feed tank average TCS concentration for the former experiment was measured as 747 ppb at time zero. A solution of TCS was spiked to the feed tank as to give TCS concentration of 750 ppb (theoretically). Deviation between theoretically calculated and measured values is 0.4% which could be taken as acceptable, considering the sensitivity of the measuring method. Similarly, in second set of experiment conducted without membrane, spiked amount of TCS (1250 ppb) was measured as 1265 ppb. (Table 8, Table 9).

As seen from Table 8, TCS concentration decreased from 747 ppb (average of two parallel measurements) to 150 ppb in the first 10 hours. Similarly, Table 9 depicts first ten hours decrease of TCS concentration from 1268 ppb to 333 ppb. These observations clearly show that, even without membrane in the system, TCS concentration declined remarkably.

Table 8 TCS Change in Feed Tank of filtration set-up, without membrane (C0=750 ppb)

Time (h)	Feed Tank TCS Concentration (ppb) (Measurement 1)	Feed Tank TCS Concentration (ppb) (Measurement 2)	Average Feed Tank TCS Concentration (ppb)
0	759	734	747
1	740	688	714
2	420	389	405
3	379	376	378
4	390		390
5	257	257	257
6	229		229
7	202	199	200
8	196		196
9	189	189	189
10	152	149	150
20	134		134
22	88		88
24	70	68	69
26	67		67
38	63	64	64
42	78	97	87
46	82		82
120	36	45	40

Table 9 TCS Change in Feed Tank of filtration set-up, without membrane (C_0=1250 ppb)

Time (h)	Feed Tank TCS Concentration (ppb) (Measurement 1)	Feed Tank TCS Concentration (ppb) (Measurement 2)	Feed Tank TCS Concentration (ppb) (Average)
0	1275	1261	1268
1	1155	1162	1158
2	989	997	993
3	818	824	821
4	666	632	649
5	536	535	536
6	468	479	474
7	399	392	395
8	381	368	374
9	375	366	370
10	352	314	333
20	338		338
22	352	366	359
24	288		288
26	278	275	277
38	265	260	263
42	239	243	241
46	243		243
120	239	237	238

Here, one should notice that feed tank is closed and not transparent so that sunlight could not penetrate into it. Hence, the possibility of decomposition of the TCS by sunlight was eliminated. Also, there was not any decrease in the raw water level in the feed tank, so evaporation of the TCS was not the case. One other possible reason to observe TCS decline could be the adsorption of TCS onto the inner surfaces of the feed tank, installation tubes etc., In order to determine if such occurrence exists, adsorption behavior of TCS onto Teflon material was explored as stated in the following section.

3.10. Adsorption Behavior of TCS

In an attempt to understand the cause(s) for the TCS concentration decrease in the feed water tank two sets of adsorption experiments were performed. In these experiments, adsorption behavior of TCS onto Teflon material was sought. The reason for selecting a Teflon material to test was the known low potential of Teflon as adsorbent [57]. Considering the feed tank, pipings and installation tube(s) materials comparison of the results obtained with Teflon and the system itself would give, at least, an idea about the extent of adsorption in the system. To that purpose, time course variation of TCS concentration was monitored in the Kesikköprü raw water placed in Teflon crucibles. In order to see the effect of temperature on adsorption behavior of TCS onto Teflon surface, two sets of experiments, one at 19±2 ^{0}C (i.e. room temperature condition), the other one at 40C (i.e. refrigerator condition) were conducted. Data obtained are shown in the Table 10. Initially 1250 ppb concentration was measured as 1375 and 1366 ppb for Teflon crucibles at 19 ^{0}C and +4 ^{0}C, respectively. In the first 10 hour of experiment (Table 10) TCS concentration decreased from 1375 to 916 ppb which is 33% reduction for 190C. On the other hand at +4 ^{0}C, TCS concentration decreases from 1366 ppb to 1046 ppb which is 23% reduction in concentration. These observations indicated that temperature difference also affects the TCS concentration reduction in Teflon crucibles.

After 10 hours of this experiment, samples were stored in refrigerator and at time 120 again TCS was measured. At time 120th hour, TCS concentration remained at these concentrations (i.e. 1220 and 1026 ppb for samples at 19 ^{0}C and +4 ^{0}C, respectively).

Table 10 Change in TCS Concentration in Solution in Teflon Crucible wrt.

Time (h)	TCS concentration change In Teflon (@+19^{0}C) C_0=1250ppb)	TCS concentration change In Teflon (@+ 4 ^{0}C) (C_0=1250ppb)
0	1375	1366
1	1258	1337
2	1137	1375
3	1165	1321
4	1160	1308
5	1165	1090
6	975	929
7	1032	908
8	954	867
9	924	1055
10	916	1046
120	1220	1026

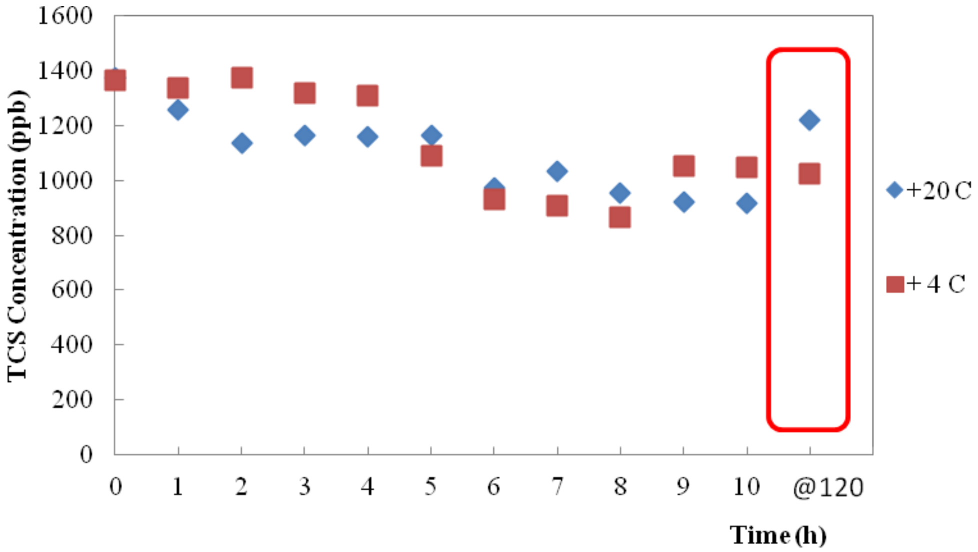

Figure 8 Change in TCS Concentrations of the Solutions in Teflon.

Results of above mentioned two experiments and result of experiment without membrane in Table 9 were normalized with respect to surface area that could affect the adsorption of TCS onto the surface and then were compared. Relevant data are presented in Table 11. As seen from this table, adsorption of TCS per unit area for the filtration system is much more than for the Teflon crucible at the same temperature. Hence, it can be stated that appreciable TCS adsorption onto the inner surfaces of the filtration system feed tank, tubing etc. is taking place, evidently.

As also shown in Table 11, adsorption per unit area for the system itself (i.e.13.99mg/m2) is much higher than that on teflon (i.e.5.99 and 4.20 mg/m2 for +19 ^{0}C and +4 ^{0}C respectively).

Table 11 Adsorption onto Teflon Experiment TCS Initial Concentration 1250ppb and System feed tank (Initial TCS concentration:1250ppb)

	Teflon Adsorption (@+19^{0}C)*	Teflon Adsorption (@+ 4 ^{0}C)*	NF System (feed tank, tubings, etc.) w/out Membrane
Surface Area (m^2)	0.0137	0.0137	0.3343
Volume (L) of solution	0.147	0.147	5
Volume (L) remained	0.137	0.137	4.99
TCS Concentration @t=0(h) (ppb)	1375	1366	1268
TCS Concentration @ t=10(h) (ppb)	916	1046	333
Mass of TCS at t=0h (mg)	0.20	0.20	6.34
Mass of TCS at t=10 h (mg)	0.13	0.14	1.66
Mass of TCS Adsorbed (mg)	0.07	0.06	4.68
TCS adsorption per unit area (mg/m^2)	5.59	4.20	13.99

*conducted in crucibles

3.11. TCS Removal by DK-NF Membrane (Set 4)

In the light of findings presented in 3.9 and Sec. 3.10, a new operational strategy was employed in the following experiments to exclude the TCS adsorption onto the filtration system only and, in a way, to determine the TCS removal by nanofiltration process itself.

Desired TCS concentration (i.e. 5000ppb) was spiked to the raw water in the feed tank and experiment system was let to operate. It was observed that TCS concentration in the feed tank decreased with time, as expected, because of the adsorption of TCS onto the system's feed tank and pipings etc. Therefore, this part of the experiment was called as "system adsorption". At this stage there was no membrane in the system, so removal was due to the adsorption of the TCS to the system only.

When TCS concentration in the feed water becomes stable, membrane was placed to its holder in the system. Again samples were taken from influent (feed water) and effluent (permeate) and were analyzed in terms of TCS concentration. During the experiment, permeate flux readings were taken and stability of the membrane was monitored accordingly.

In this set of experiment, TCS was spiked into the raw water at a concentration of 5000 ppb. Uncompacted "DK-NF" membrane was utilized. Experiment was conducted at 6.9 bar pressure and 1.2 m/sec cross-flow velocity. Temperature of the feed water was kept at 19±2 ^{0}C. 5 liters of Kesikköprü raw water was utilized for this set of experiment. System was operated without a membrane for about 24 hours in order to be able to exclude the system adsorption effect on performance evaluation of nanofiltration process.

Steady-state flux values were 53.6 L/m2.h, 43.0 L/m2.h, 51.2 L/m2.h and 48.7L/m2.h, for clean water flux before raw water (Jcwi), raw water flux (Jrw), clean water flux before cleaning (Jcws) and clean water flux after cleaning (Jcwc), respectively. In an attempt to investigate the flux performance of the membrane, flux data presented in Figure 9 was collected.

If there exists any fouling, one would detect this from the flux data. Also, these flux data would indicate whether fouling is reversible or irreversible.

In this set, irreversible fouling was calculated as 4.5%. Although there seems to be some irreversible fouling, this fouling value is not so much and it could be accepted in the range of experimental error. Another point to mention is the cleaned water flux before raw water, Jcwi, (53.6 L/m2.h) which decreased to 43 L/m2.h with the raw water flux. This is an expected observation as the ingredients present in the raw water would clog the pores leading to a decrease in the flux.

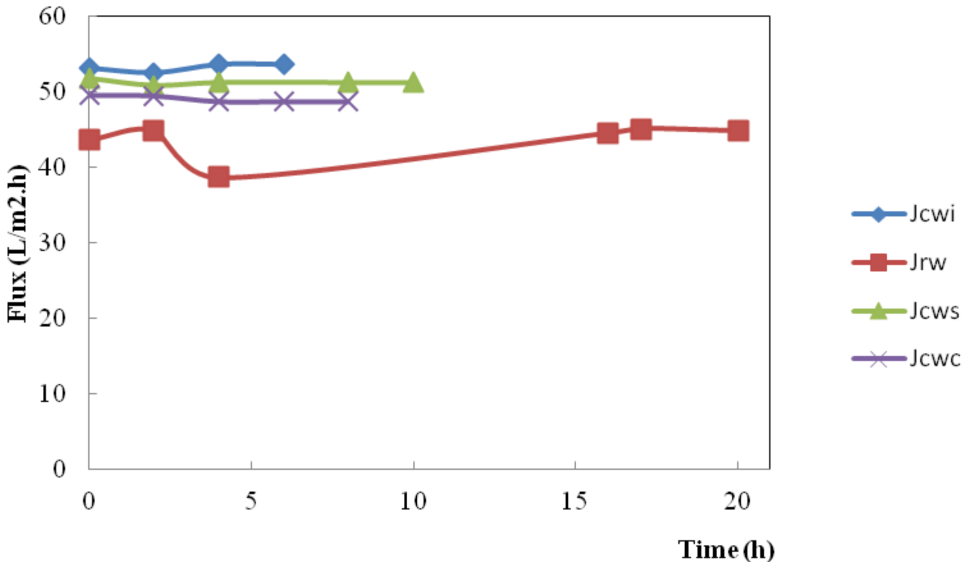

Figure 9 Flux variation for DK-NF membrane (Set 4) (TMP: 6.9 bar; CFV: 1.2 m/sec)

In Table 12, water flux, flux decline and total fouling values at steady-state are presented. As seen from this table, flux decline was about 20%, which was thought to be mainly caused by TCS and natural organic matter (NOM) present originally in the raw water. This flux decline was partly irreversible, though not much (only 4.5 %), because of pore blocking and adsorption of TCS and NOM on the membrane surface. However 4.5 % irreversible fouling could be in the range of experimental error. While, flux recovery was quite high with a value of 95.5%.

Table 12 Water flux, flux decline and total fouling for DK-NF membrane (TMP:6.9 bar; CFV: 1.2 m/sec) (Set 4)

Clean Water Flux Before Raw water (J_{cwi}) ($L/m^2.h$)	53.6
Raw Water Flux (J_{rw}) ($L/m^2.h$)	43.0
Clean Water Flux After Cleaning (J_{cwc}) ($L/m^2.h$)	48.7
Flux recovery (%)	95.5
Flux Decline (%)	19.8
Irreversible Fouling (%)	4.5

Regarding the TCS removal, the results obtained are presented in Table 13 and Table 14, for the “system adsorption” part and “nanofiltration” part, respectively. As seen from Table 13, TCS concentration in the feed tank gradually decreased from 4626 ppb to 1865 ppb within 20 h, which means around 60% of the TCS was removed without having a membrane in the system. For the following 4 hours of experimentation, TCS value was stable around 1850 ppb. So the system was considered as saturated with TCS and nanofiltration test was initiated. The results obtained during the nanofiltration part of the experiment are given in Table 14. As indicated, although the initial TCS concentration was 1879 ppb, after 46 hours, TCS concentration in the influent decreased to 1160 ppb. This corresponds to about 38% further reduction in the feed water TCS concentration. This could be because of adsorption of TCS onto the membrane surface.

TCS removal efficiency of the membrane filtration was not very promising with a value of around 20-30% (Figure 10). In fact, it should be mentioned that it is of possibility to misinterpret the TCS removal data presented in Table 13 and Table 14. Because, considering influent and effluent TCS concentrations of 1879 ppb and 283 ppb, respectively, at time zero (Table 14), TCS removal efficiency would be estimated as 85%. But, this would not be correct as the steady state has not been reached yet at this time. However, at 46th hour of nanofiltration, where a steady state was reached, the influent and effluent TCS concentrations were 1160 ppb and 798 ppb, respectively, which correspond to 31% TCS removal. On the other hand, if conventional calculation method was applied as such, that initial feed TCS concentration was 4626 ppb at the very beginning of the experiment and it was decreased finally to 798 ppb, then TCS removal efficiency would be found as 82%. This is a quite promising result for nanofiltration, however considering the fact that filtration system adsorbs some TCS it is not the true performance value of the membrane to report indeed, and the removal efficiency of nanofiltration for his set of experiment was only 31%, as shown in Figure 10.

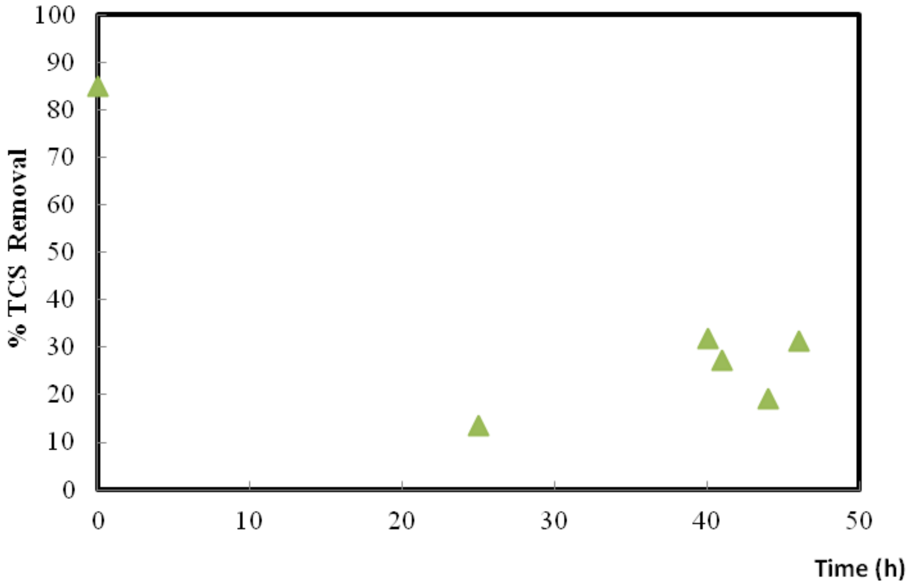

Figure 10 Triclosan Removal Efficiency vs. time for DK-NF membrane at 6.9 bar pressure (Set 4)

Table 13 TCS variation in the feed tank during the "System Adsorption" part of the experiment (TCS C0=5000ppb) (Set 4)

Time (h)	Feed Tank 1	Feed Tank 2	Average Feed Tank
0	4628	4625	4626
2	3221	3150	3186
4	2753	2724	2739
10	1929	1971	1950
20	1858	1872	1865
23	1855	1864	1859
24	1829	1858	1844

Table 14 Influent and effluent TCS variations during the “Nanofiltration Part” of the experiment (Set 4)

Time (h)	Influent 1* (ppb)	Influent 2* (ppb)	Average Influent (ppb)	Effluent 1* (ppb)	Effluent 2* (ppb)	Average Effluent (ppb)	% Removal
0	1886	1872	1879	248	319	283	85
2	1287	1406	1346				
4	1230	1202	1216	1241	1224	1233	
6	1344	900	1122				
20				1014	898	956	
25		1673	1673	1537	1355	1446	14
27				1622	1417	1520	
40	1327	1193	1260	818	898	858	32
41	1057	1114	1085	846	730	788	27
43				721	750	736	
44	1122	1062	1092	889	878	883	19
46	1145	1176	1160	818	778	798	31

*Parallel measurements.

3.12. Effect of NOM Content on TCS Removal by Nanofiltration

In an attempt to understand the effect of NOM content of raw water on TCS removal, three different experimental sets, namely Set 5, 6 and 7 were designed and put into operation. The possible effect of NOM, beside TCS, on the flux values of the system will be illustrated. Moreover, NOM in the raw water could interact with TCS during nanofiltration. Different NOM levels (10 and 26 mg/L in terms of TOC) were obtained by spiking a humic acid (HA) solution into the raw water containing TCS at two different concentrations (2500 and 5000 ppb). Following subsections belong to these experiments.

4.5.1. Set 5:2500ppb TCS + 10 mg/L HA

In this set of experiment HA was spiked to the feed tank as to give 10 mg/L as TOC in feed solution as soon as membrane was placed to its holder in the system (for Set 6 and 7 humic acid was spiked at "nanofiltration part" when stable TCS concentration observed). As discussed earlier, prior to nanofiltration part, the system was saturated with TCS during the "system adsorption part" in which spiked TCS concentration was 2500 ppb.

Flux values observed are presented in Figure 11. As seen from this figure, steady-state flux values were 36 L/m2.h, 28.3 L/m2.h, 36.4 L/m2.h and 40.2 L/m2.h for clean water flux before raw water (Jcwi), raw water flux (Jrw), clean water flux before cleaning (Jcws) and clean water flux after cleaning (Jcwc), respectively.

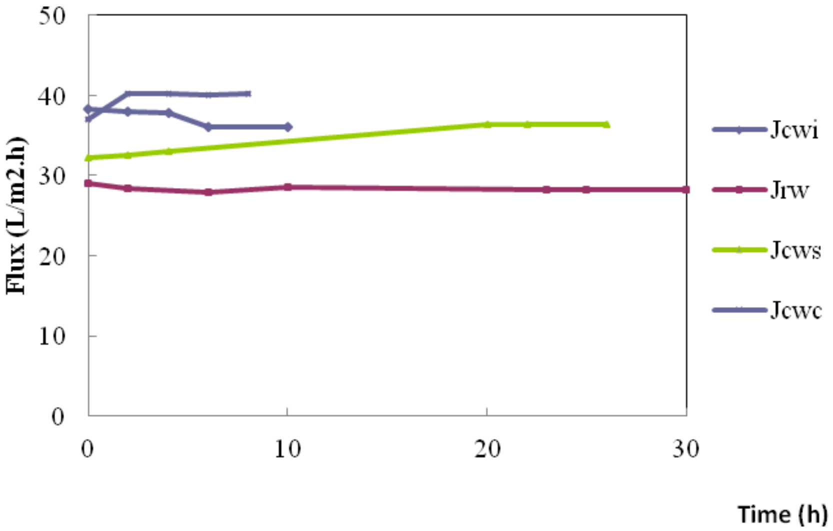

Figure 11 Flux values vs time for DK-NF membrane –"nanofiltration part" with 10 mg/L humic acid (Set 5) (TMP: 6.9 bar; CFV:1.2 m/s, TCS C_0: 2500 ppb)

In Table 15, steady state water flux, flux decline and total fouling values are presented. As seen from this table, no irreversible fouling was observed despite the humic acid addition to the feed tank. Steady state flux value for raw water was 28.3 L/m2.h which is lower than clean water flux before raw water (Jcwi)(i.e.,36 L/m2.h). Hence, as expected, flux decrease was observed in this set of experiment and, on the contrary, clean water flux after cleaning (Jcwc) was recovered by more than 100%. This could be due to pore expansion, swelling of the membrane. This swelling might occured due to compaction was not applied in set 5.

Table 15 Water flux, flux decline and total fouling for DK-NF (Humic Acid: 10 mg/L as TOC, TMP:6.9 bar; CFV:1.2 m/sec; TCS C0:2500ppb) (Set 5)

Clean Water Flux Before Raw water (J_{cwi}) ($L/m^2.h$)	36.0
Raw Water Flux (J_{rw}) ($L/m^2.h$)	28.3
Clean Water Flux After Cleaning (J_{cwc}) ($L/m^2.h$)	40.2
Flux Recovery (%)	101.2
Flux Decline (%)	21.4
Irreversible Fouling (%)	No Fouling

Table 16 TCS variation in the feed tank during "System Adsorption" part of the experiment (TCS C0=2500ppb) (Set 5)

	TCS Concentration(ppb)		
Time (h)	Feed Tank 1*	Feed Tank 2*	Average Feed Tank
0	1953	1710	1831
2	827	856	842
4	524	529	527
10	444	440	442
20	382	378	380
23	378	376	377
25	376	371	373

* parallel measurements from the same feed tank

Spiked TCS concentration in the feed tank was 2500 ppb. However, TCS concentration in the sample taken from the feed tank at time zero was measured as 1831 ppb on average. This deviation in TCS concentration measurement can be attributed to surface adsorption of TCS onto the lab ware. At the 25th hour of experiment, TCS concentration in the feed tank stabilized at 373 ppb. At this point, DK-NF membrane was placed to its holder in the system, and concurrently, humic acid was spiked to the feed tank at a concentration of 10 mg/L. Simultaneously, it was observed that TCS concentration in the effluent dropped down to a level below LOQ which was determined to be 28 ppb, even just right after the introduction of humic acid into the system. This corresponds to >93% and >80% TCS removal efficiency at time zero and 20 h, respectively (Figure 12 and Table 17). This removal efficiency is comparably higher than that obtained in the former set of experiment (i.e. 31%) (Set 4). This increase in the removal efficiency was attributed to the presence of humic acid in the raw water. Probably, the humic acid formed a layer on the surface of the membrane, in a way, increased the TCS rejection. On the other hand, as stated earlier, flux values displayed an expansion in the membrane; so, one would expect to observe a decrease in TCS removal efficiency. This can be easily inferred from the comparison of the influent TCS results recorded with and without humic acid (Table 17 and Table 14, respectively) , In the absence of externally added humic acid, during nanofiltration part, initial influent TCS concentration was 1879 ppb which decreased to 1160 at the end of experiment, which means 38% decrease (Table 14). On the other hand, in the presence of externally added humic acid, the corresponding TCS concentrations were 375 ppb and 141 ppb, which reflect 62 % TCS reduction in the feed water. This could indicate the possible clogging of the membrane by the humic acid. As mentioned in Kimura's study, TCS is hydrophobic and likely to adsorb onto NF/RO membranes [8]. Accordingly, decrease in TCS concentration can be attributed to adsorption onto the membrane itself. And also same author mention that tested membrane should be saturated with compounds to be removed or with NOM as applied in this study.

From the foregoing discussion, it can be understood that flux behavior of the membrane was not consistent with its TCS removal behavior. Due to this inconsistency, this set was repeated with some modifications, as given in the following section.

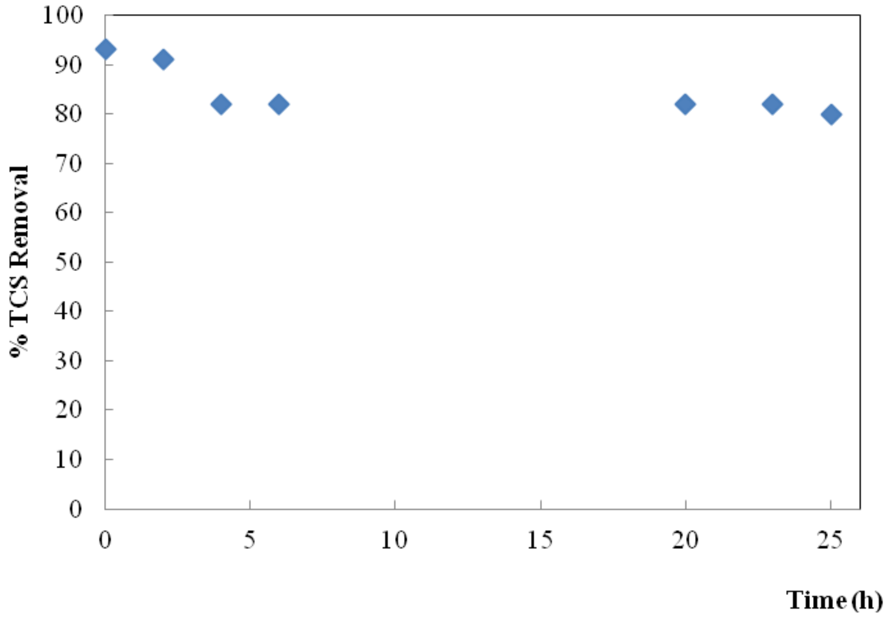

Figure 12 Triclosan Removal Efficiency for DK-NF membrane during "nanofiltration" part of Set 5 (TMP:6.9 bar; CFV: 1.2 m/sec; TCS C0: 2500 ppb)

Table 17 Influent and effluent TCS variation during the "Nanofiltration Part" (HA:10 mg/L as TOC)

Time (h)	Influent 1	Influent 2	Average Inf.	Effluent 1	Effluent 2	Average Eff.	% Removal
0	376	374	375	<LOQ*	<LOQ	<LOQ	>93
2	297	308	302	<LOQ	<LOQ	<LOQ	>91
4	164	155	160	<LOQ	<LOQ	<LOQ	>82
6	157	150	153	<LOQ	<LOQ	<LOQ	>82
20	159	157	158	<LOQ	<LOQ	<LOQ	>82
23	156	149	152	<LOQ	<LOQ	<LOQ	>82
25	142	139	141	<LOQ	<LOQ	<LOQ	>80

* LOD = 4.3 ppb LOQ = 28 ppb

4.5.2. Set 6:5000ppb TCS + 10 mg/L HA

This set of experiment differs from Set 5 in the sense that HA was introduced to the system not as soon as membrane was placed but when stable TCS concentration was observed during nanofiltration part of the experiment. In a way, membrane was saturated with TCS before HA is introduced. Also, TCS concentration was increased to 5000 mg/L from 2500 mg/L of the previous set, in order to allow the detection of TCS in effluent samples.

Flux values observed are presented in Figure 13. Steady-state flux values were 40.8 L/m2.h, 40.2 L/m2.h, 42.6 L/m2.h and 47.1 L/m2.h for initial clean water flux, raw water flux, clean water flux before cleaning and clean water flux after cleaning is applied, respectively.

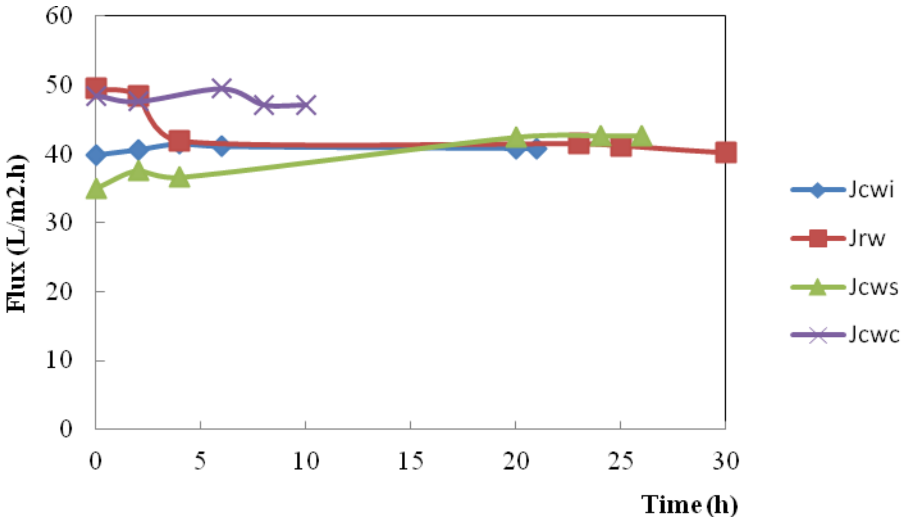

Figure 13 Flux values vs time for DK-NF membrane –"nanofiltration part" with 10 mg/L humic acid (Set 6) (TMP: 6.9 bar; CFV:1.2 m/s, TCS C_0: 5000 ppb)

In Table 18, water flux, flux decline and total fouling values at steady-state are illustrated. Clean water flux of 40.8 L/m2.h (Jcwi) decreased to 40.2 L/m2.h when raw water was applied. This tiny amount of decrease could be ignored. Flux recovery is 104.4 % . Irreversible fouling was not observed in this set. Raw water flux value stayed as it is even after humic acid addition to the system(i.e. 40.2 L/m2.h)

Table 18 Water flux, flux decline and total fouling for DK-NF (Humic Acid: 10mg/L as TOC, TMP: 6.9 bar; CFV: 1.2 m/sec.;TCS C0:5000ppb)(Set 6)

Clean Water Flux Before Raw water(J_{cwi}) (L/m^2.h)	40.8
Raw Water Flux (J_{rw}) (L/m^2.h)	40.2
Clean Water Flux After Cleaning (J_{cwc}) (L/m^2.h)	47.1
Raw Water Flux after Humic Acid addition (L/m^2.h)	40.2
Flux Recovery (%)	104.4
Flux Decline (%)	1.47
Irreversible Fouling (%)	No Fouling

During the “system adsorption” part, in which membrane is not in its holder , initial feed tank TCS concentration was measured as 5012 ppb whereas at 22nd hour of the experiment it was measured as 1088 ppb (Table 19). Decrease in the feed tank TCS concentration by 78% was observed without membrane in the system.

As depicted in Table 20, during the nanofiltration part of the experiment, system reached to steady state at 33rd hour (flux values are presented in appendix Table A-14 Raw water Flux (C0=5000ppb TCS))and at that time, TCS removal efficiency was as attained as 60%. As soon as a steady state was reached, HA was spiked to the feed tank (at 10 mg/L as TOC). Following the addition of HA into the feed tank, removal efficiency did not change much, keeping at around 59%. This shows that 10 mg/L HA addition did not change the TCS removal efficiency, as contrary to findings of Set 5 where > 80% TCS removal was evident.. However, as compared to the results obtained in Set 4 where no HA is present (31% TCS removal), TCS removal performance was much better. Then, it was decided to increase the HA concentration to investigate the effect of HA concentration on TCS removal and to clarify the picture. To that purpose, HA added was increased as to give a total TOC of 26 mg/L in the feed water in the subsequent experimental set by keeping the other parameters the same.

Table 19 TCS variation in the feed tank during "System Adsorption" part of the experiment (TCS C0=5000ppb) (Set 6)

	Concentrations(ppb)		
Time (h)	Feed Tank 1	Feed Tank 2	Average Feed Tank
0	4937	5086	5012
4	4423	4478	4450
21	1156	1166	1161
22	1077	1099	1088

Table 20 Influent and effluent TCS variation during the "Nanofiltration Part" (HA:10 mg/L as TOC)

HA addition	Time (h)	Influent TCS (ppb) Average of two measurements	Effluent TCS (ppb) Average of two measurements	% TCS Removal
No	0	1088		
No	4	670		
No	33	456	179	60%
Yes	34	448		
Yes	53	370	150	59%

Regarding the TOC removal performance of nanofiltration, influent and effluent TOC values were monitored during the entire process. TOC measurements were conducted via UVA254 measurements. Original raw water TOC value was around 2.8±0.3 ppm.. When HA was spiked into the raw water, TOC concentration in feed water became 10±0.1 mg/L as shown in Table 21. TOC removal efficiency attained was 76 % which is higher than TCS removal. Before addition of HA into the feed tank, TOC removal percentage was around 20 % however addition of HA resulted in increase in the TOC removal efficiency (Table 21). This observation was attributed to the effect of HA adsorbed onto the surface of membrane and therefore removal efficiency of TOC increased.

Table 21 TOC removal (Set 6)

HA addition	Time (h)	TOC Influent (mg/L) (average of two measurements)	TOC Effluent (mg/L) (average of two measurements)	% TOC Removal
No	0	2.83	2.30	18.7
No	4	2.85	2.30	19.3
No	6	2.82	2.30	18.4
No	13	2.83	2.30	18.7
No	33	2.91	2.29	21.3
Yes	33	8.12	2.34	71.2
Yes	36	10.10	2.26	77.6
Yes	56	9.56	2.21	76.9

4.5.3. Set 7:5000ppb TCS + 26 mg/L HA

This set of experiment was the same with Set 6 experiments except the spiked HA concentration. HA concentration was increased to 26 mg /L as TOC to investigate the effect of HA concentration on the TCS removal efficiency of nanofiltration. Pressure and CFV were adjusted to 6.9 bar and 1.2 m/s, respectively and the raw water sample was pretreated as in the preceding sets of experiments.

Flux values observed are presented in Figure 14. Steady-state flux values were measured as 58.2 L/m2.h, 55.4 L/m2.h, 55.9 L/m2.h and 57.9 L/m2.h for initial clean water flux, raw water flux, clean water flux before cleaning and clean water flux after cleaning is applied, respectively.

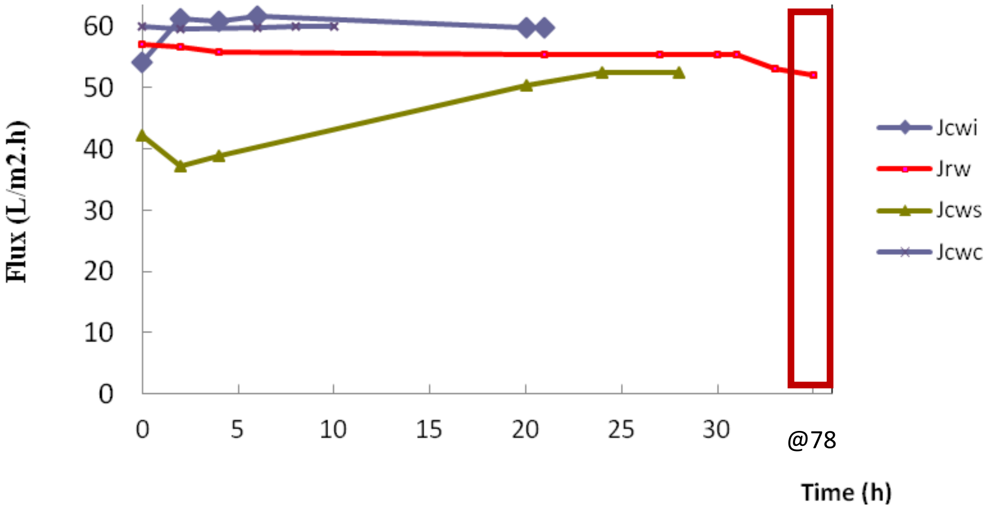

Figure 14 Flux values vs time for DK-NF membrane –"nanofiltration part" with 26 mg/L humic acid (Set 7) (TMP: 6.9 bar; CFV:1.2 m/s, TCS C_0: 5000 ppb)

In Table 22, water flux, flux decline and total fouling values at steady-state are presented. Clean water flux of 58.2 L/m2.h (Jcwi) decreased to 46.9 L/m2.h when raw water was applied. This could be due to pore blocking since clean water flux after cleaning (Jcwc) value is higher than Raw Water Flux (Jrw) with a flux recovery of 96%. Decrease in raw water flux was the case for the initial part of the set while addition of HA decreased the flux during raw water passage as such that steady state flux value for the raw water was 46.9 (L/m2.h) while initially it was around 51 (L/m2.h)

Table 22 Water flux, flux decline and total fouling for DK-NF membrane (Humic Acid:26mg/L as TOC, TMP:6.9 bar; CFV:1.2 m/sec, TCS C0:5000ppb)(Set 7)

Clean Water Flux Before Raw water(J_{cwi}) (L/m^2.h)	58.2
Raw Water Flux (J_{rw}) (L/m^2.h)	55.4
Raw water Flux (L/m^2.h) after HA adition	46.9
Clean Water Flux After Cleaning (J_{cwc}) (L/m^2.h)	57.9
Raw Water Flux after Humic Acid addition (L/m^2.h)	46.9
Flux Recovery (%)	96.2
Flux Decline (%)	4.8
Irreversible Fouling (%)	3.9

TOC values calculated via UVA254 measurements were around 5±0.1 ppm (feed water) during the “system adsorption” part (Table 25). In the previous set (i.e. Set 6), this value was around 2.8 mg/L. In fact, one should not expect such difference to observe as the same raw water sample was used in both sets. However, this was the case. This increase in the TOC content of the feed water could be due to the residues of HA remaining in the pores and on surface of the membrane from previous set (Set 6) despite a cleaning procedure was applied prior to Set 7. Following the system adsorption part, membrane was placed into the its holder and nanofiltration experiment was commenced. HA addition was accomplished when the stable TCS concentration was observed during nanofiltration part of the experiment. As soon as HA was spiked into the feed tank, TOC level increased to 25.72 mg/L as shown in Table 26.

Table 23 presents the TCS variation in the feed tank during the “system adsorption” part which took about 22 hours. As can be inferred from this table, decrease in the feed tank TCS concentration was by 72.7 % .

In the nanofiltration part of this set, as seen from Table 24, the system reached the steady state at 33rd hour with a TCS removal efficiency of 63%. This was in accordance with the observation in Set 6 (60%). Then, HA was spiked to the feed tank and it was observed that the TCs removal efficiency did increase to 75%, unlike in Set 6 where TCS removal did not change (59%). However, when this observation is evaluated together with the TCS removal performances of Set 4, 5 and 6, it would be possible to state that HA has a positive effect on the TCS removal by nanofiltration. This positive effect of HA could be due to the fouling of the membrane by HA which, in turn, increases the TCS removal efficiency..

Increasing HA level resulted in not only increase in TCS removal efficiency but also TOC removal efficiency. In this set, TOC removal efficiency rise up to 90 % from %76 of Set 6. This clearly illustrates that increasing NOM level results in increase in both TCS and TOC removal

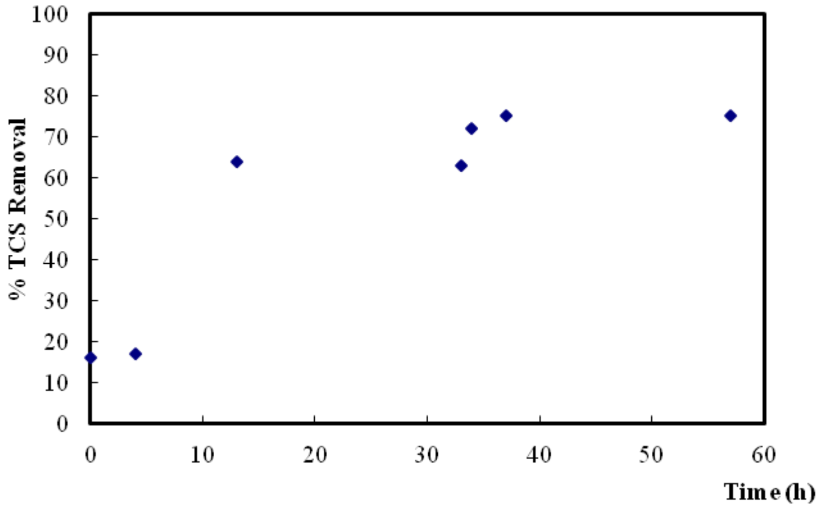

Figure 15 Triclosan Removal Efficiency for DK-NF membrane during "nanofiltration" part of Set 7 (TMP:6.9 bar; CFV: 1.2 m/sec; TCS C0: 5000 ppb)

Table 23 TCS variation in the feed tank during "System Adsorption" part of the experiment (TCS C0=5000ppb) (Set 7)

	Concentrations(ppb)		
Time (h)	Feed Tank (Measurement 1)*	Feed Tank (Measurement 2)*	Average Feed Tank
0	4926	4917	4922
4	3188	3192	3190
21	1312	1365	1339
22	1340	1341	1340

*parallel measurements

Table 24 Influent and effluent TCS variation during the "Nanofiltration Part" (HA:26 mg/L as TOC)

		Concentrations(ppb)		
HA addition	Time (h)	Influent (average of two measurements)	Effluent (average of two measurements)	% Removal
No	0	1339±1	1120±25	16
No	4	1227±2	1017±10	17
No	6	955±2		
No	13	922±2	333±1	64
No	33	891±2	327±6	63
Yes	34	249±2	70±4	72
Yes	37	246±2	62±1	75
Yes	57	241±2	61±1	75

During system adsorption part of the experiment although there are fluctuations in TOC level, there is not much difference between C0 and final concentration.

Table 25 TOC variation in the feed tank during "System Adsorption" part of the experiment (Set 7)

Time (h)	TOC Feed Tank (ppb)
0	5.25
2	5.27
8	5.21
24	5.08
26	5.14
27	5.10

Table 26 TOC removal

Time (h)	TOC Influent (ppb)	TOC (ppb) Effluent
0	25.72	10.04
3	24.43	8.71
18	25.22	8.60
30	24.77	2.41
31	25.19	2.42
32	25.42	2.42
38	25.80	2.42

CHAPTER 5

DISCUSSION

In an attempt to discuss the results presented in Sec 4 and in a way, to clarify the picture, the results obtained through the experimental sets were analyzed in a comparative way. In Table 27, summary of the results obtained during the system adsorption parts of the study is presented. In this table, initially spiked TCS concentration (intended) and measured TCS concentration values are illustrated. TCS concentrations after system adsorption are also shown. Percentage of TCS adsorbed by the installation stuffs (pipe, valves, feed tank etc.) of the system only (total "system adsorption" percentage) can also be depicted from this table. As seen from Table 27, TCS adsorption onto the system varied between 60.1 and 94.6 %, through the sets. It seems that the initial TCS concentration is the major factor affecting this variation; the lower the initial TCS concentration, the higher the percentage of TCS adsorbed by the system.

So, considering this system adsorption fact, while determining the TCS removal efficiency of nanofiltration system, the stabilized TCS concentration in the feed tank attained in the absence of membrane, should be consider as the initial TCS concentration.

One point that needs to be mentioned here is that there occurred a considerable difference between the intended and measured initial TCS concentration in Set 5 (2500 vs 1831 ppb), which might have affected the total system adsorption calculation. The reason for this difference is thought to be due to switching from LC/MS-MS to HPLC to measure the TCS concentrations in Set 5. However, after a series of measurements, the HPLC method was stabilized and more accurate results were obtained for the rest of the experiments, as seen for the rest of the sets in Table 27.

Table 27 Overview of the results belonging to the "system adsorption" part of the experiments

	Feed water TCS , ppb (intended)	Feed water TCS ,ppb (measured) (K)	TCS after "system adsorption",ppb (L)	Total System Adsorption (%) [(K-L)/K)*100]
Set2	750	747	40	94.6
Set3	1250	1268	238	81.2
Set4	5000	4626	1844	60.1
Set5	2500	1831	373	79.6
Set6	5000	5012	1088	78.3
Set7	5000	4922	1340	72.8

3.13. TCS Removal Efficiency Comparison

Rejection of solutes in the liquid phase by the membrane is governed by two main mechanisms namely size exclusion (sieving) and electrostatic repulsion. [58] Main principle in size exclusion is penetration ability of solute among the pores of the membrane. Relatively smaller size solute could pass through the pores on the other hand larger size solute are kept on the membrane surface and this result in as a removal or the larger size solute in membrane process. While electrostatic repulsion of the solute is governed due to charge interaction between membrane and solute. Basic physical principle of similar repels and opposites attract plays an active role at that stage. As a result these two principles govern the rejection mechanisms in membrane filtration process.

Table 28 presents the overall TCS removals attained in different sets of experiments and provides a general comparison. In Set 4, there were no HA (except the originally present in the raw water as NOM) in the system and the overall TCS removal was around 57.5 %. Addition of HA increased overall TCS removal percentages in Sets 5, 6 and 7.

For Set 7, overall TCS concentration was 95.4% which was the highest removal efficiency attained (Table 28). When compared with Set 6, removal percentage increased by about 10% with the increase in HA content of the raw water (HA concentration for Set 6 is 10 mg/L and for Set 7 is 26 mg/L as TOC)

Table 28 Overall TCS Removals attained

	TCS right after membrane is placed in system (ppb)	TCS concentration when experiment is finalized (ppb)	Overall TCS Removal (%)
Set4	1879	798	57.5
Set5	375	28	92.5
Set6	1088	150	86.2
Set7	1339	61	95.4

During total removal calculation of TCS in Table 29 “A” was taken as TCS influent concentration as soon as membrane placed (ppb) and “B” was taken as TCS effluent concentration at steady state (ppb). “A” gives the initial TCS concentration at the beginning of the treatment part because membrane was introduced to the system at that time and “B” stands for the final TCS concentration at the end of experiment. Hence percentage difference of these two data gave the total removal of TCS in the system. On the other hand membrane sieving consists of the difference of influent and effluent concentration at steady state (i.e. “C” and “B” which are TCS influent and effluent concentrations at steady state (ppb), respectively) At this stage membrane was included in the system and it was saturated with the compound that we want to remove from water namely TCS. Summary tables (Table 29 and Table 30) presenting the contribution of these removal mechanisms to the overall TCS removal are prepared.

While comparing the total removal efficiency of nanofiltration membrane for Set 5 and Set 4 (Table 29), it was observed that removal percentage for Set 5 (i.e., 92.5%) is higher than removal percentage of Set 4 (i.e., 57.5%). This is mostly due to the HA in the feed water. Namely, in Set 4 there were no HA in the system (except originally present NOM in the raw water) however Set 5 includes the spiked HA as to give 10 mg/L as TOC, in the feed water. Total removal percentage for Set 5 includes HA effect on TCS removal, so adding HA increased the removal efficiency of membrane.

In case of Set 6 and 7, similar results were obtained (i.e., 83.5 and 75.6%, respectively)(Table 29). These values were less than that in Set 5 in which HA was spiked as soon as membrane was placed while in Set 6 and 7, HA was spiked after a stable TCS concentration was established. Total TCS removal value for Set 5 (i.e.,92.5%) includes the HA adsorption. However, total removal percentage value for Set 6 and 7 did not include the HA adsorption effect.

TCS removal by membrane sieving mechanism for Set 4 was determined to be 31.2% and this value increased to 60.7 and 63.3% for Set 6 and 7, respectively (Table 29). Removal percentage (i.e., 80.1%) by membrane sieving for Set 5 includes HA addition, so this value is much higher than the sieving values of the other sets namely Set 4, Set 6 and Set 7. Compaction of the membrane in Set 6 and Set 7 could have resulted increase in membrane sieving (from 31.2 % for Set 4 to 60.7 % Set 6 and 63.3 % for Set 7).Compaction possibly made the membrane tighter. Another reason of this increase could be due to the employment of fresh membranes in some of the sets.

Adsorption of TCS by membrane for Set 6 and 7 was determined to be 58.1 and 33.5%, respectively (Table 29). This decrease in the adsorption of membrane could be due to the saturation of the membrane with TCS in set 6. In other words, in Set 6 and Set 7 the same membrane was utilized and spiked TCS could be deposited on the membrane and this could not be removed by chemical cleaning. Hence, decrease in the membrane adsorption was observed. Different initial concentration of Set 6 and Set 7 (1088 ppb and 1340 ppb, respectively) as soon as membrane placed could also lead to such decrease in the membrane adsorption.

TCS removal by membrane sieving mechanism for the HA adsorption part for Set 6 and 7 were 59.5 and 74.7 %, respectively (Table 30). On the other hand, membrane sieving value before HA was added for Set 6 and 7 were 60.7 and 63.3, respectively (Table 29). There is not so much difference for Set 6 (60.7 vs 59.5%), however sieving capacity of the membrane increased from 63.3 to 74.7 % (Table 29 and). This increase in sieving capacity of the membrane could be due to clogging of the pores of the membrane with HA, hence, more TCS was rejected.

Table 29 Overview of the results belonging to the nanofiltration part of experimental sets before adding the HA

	Feed water TCS , ppb intended & (measured)	TCS after "system adsorption", ppb	A	B	C	Total Removal (%) [(A-B)/A)x100]	Membrane Sieving (%) [(C-B)/C)x100]	Membrane Adsorption (%) [(A-C)/A)x 100]
Set4	5000 (4626)	1844	1879	798	1160	57.5	31.2	38.3
Set5	2500 (1831)	373	375	28	141	>92.5	>80.1**	62.4*
Set6	5000 (5012)	1088	1088	179	456	83.5	60.7	58.1
Set7	5000 (4922)	1340	1339	327	891	75.6	63.3	33.5

*membrane adsorption together with humic acid adsorption
**membrane sieving together with humic acid adsorption
A: TCS influent concentration as soon as membrane placed (ppb)
B: TCS effluent concentration @steady state (ppb)
C: TCS influent concentration @steady state (ppb)

Increase in HA concentration, increased the TCS removal by membrane adsorption (Table 30). This could be due to the possible adsorption of HA onto the membrane surface, which facilitated the adsorption of TCS on the HA layer on the membrane (i.e. HA+membrane adsorption) (Table 30, Humic Acid+membrane adsorption (%) Set6= 18.9 and Set7 =73.0). Hence, total TCS removal for Set 6 increased from 67.1 to 93.2 % for Set 7 (Table 30). These observations reveal that increasing spiked amount of HA (from 10 to 26 mg/L as TOC) resulted in increase in humic acid+membrane adsorption.

When compared the membrane sieving capacities it was 59.5 for Set 6 while for Set 7 it was 74.7% (Table 30). This was probably due to blocking of the membrane pores by HA, and hence, greater rejection of TCS by the membrane was observed.

Based on these results discussed above, it can be said that presence of HA in the raw water containing TCS, increases the total TCS removal by nanofiltration consistent with the literature.

Table 30 Overview of the results belonging to the nanofiltration Part of Experimental sets after adding the HA

	Spiked HA Concentration as TOC(mg/L)	Feed water TCS ,ppb (measured)	X	Y	Z	Total TCS Reduction (%) **	By Membrane Sieving (%) ***	By HA + membrane Adsorption (%) ****	Raw Water Flux @ Steady State (L/m2.h)
Set5	10	1831	375	<28	141	>92.5	>80.1	62.4*	28.3
Set6	10	5012	456	150	370	67.1	59.5	18.9	40.2
Set7	26	4922	891	61	241	93.2	74.7	73.0	46.9

X: TCS influent concentration as soon as Humic Acid spiked (ppb)
Y: TCS effluent concentration @steady state (ppb)
Z: TCS influent concentration @steady state (ppb)
* membrane adsorption together with humic acid adsorption
** [(X-Y)/X)*100] ***[(Z-Y)/Z)*100] ****[(X-Z)/X)*100]

3.14. Flux Comparison

In order to be able to have a better insight on the membrane behavior, Table 31 was prepared. In this table, steady state flux values are presented. Steady state clean water fluxes before raw water, raw water fluxes and clean water fluxes before and after cleaning together with steady state flux values after the addition of HA are shown (i.e., Jcwi, Jrw, Jcws, Jcwc, respectively). Flux recovery and flux decline values are also presented.

As seen from Table 31, in Set 5 and 6, flux values were fully recovered back to their original values, but not in Set 4 and 7. This could indicate that a cake or gel layer formation occurred in Set 5 and 6. On the other hand, for Set 4 and 7, irreversible fouling, though not much, was evident. Chemical cleaning in Set 7 was effective for fouling removal (i.e., Jcwi was 58.2 and Jcwc was 57.9) so, fouling was reversible to a great extent. For Set 7, pore blocking of the membrane could be the case since chemical cleaning removed the HA in the pores and flux data nearly returned back to its original value. For Set 4, fouling could not be removed by chemical cleaning.

In Set 5, expansion of the membrane was observed and for this reason compaction was applied in Set 6 and 7. In Set 6, flux value before and after cleaning was 42.6 and 47.1 L/m2.h, respectively. This could be due to removal of the gel/cake layer of the surface of the membrane or expansion in the membrane. On the other hand, in Set 7, not so much expansion was observed and steady state clean water flux after cleaning value (i.e., 57.9 L/m2.h) returned back to steady state clean water flux value before raw water (i.e., 58.2 L/m2.h).

Table 31 Steady State Flux values for all set of experiments

	Feed water TCS, (ppb) (intended)	Feed water TCS, (ppb) (measured)	(J_{cwi}) (L/m2.h)	(J_{rw}) (L/m2.h)	(J_{cws}) (L/m2.h)	(J_{cwc}) (L/m2.h)	Steady State Flux At the end of humic acid addition (L/m2.h)	Flux Decline (%) *	Flux Recovery (%) **
Set4	5000	4626	53.6	43	51.2	48.7	-	19.8	95.5
Set5	2500	1831	36	28.3	36.4	40.2	-	21.4	101
Set6	5000	5012	40.8	40.2	42.6	47.1	40.2	1.47	104.4
Set7	5000	4922	58.2	55.4	55.9	57.9	46.9	4.8	96.0

*$[[(J_{cwi}- J_{rw})/(J_{cwi})]*100$

**$[(J_{cws})/(J_{cwi})]*100$

CHAPTER 6

CONCLUSION

This study was conducted in order to investigate the performance of the nanofiltration treatment of triclosan from surface water, namely Kesikköprü Reservoir water. Two different thin film commercially available NF membranes, namely DL-NF and DK-NF was utilized in this study. Due to the TCS removal fluctuations experienced in DL-NF membrane, DK-NF membrane was preferred for the rest of the experiments. However, it was realized that decrease in TCS feed water with time caused miscalculation of removal performance of the nanofiltration. In order to clarify this problem, two sets of experiments were conducted with filtration set-up in the absence of membrane in its holder. The results obtained illustrated that the decrease in TCS concentration in the feed water was not due to the adsorption of the TCS onto the membrane surface as was mentioned in the literature [54]. This decrease was a result of the adsorption of the TCS onto the system's inner surfaces due to hydrophobic characteristic of TCS. In order to explore this observation, TCS's adsorption behavior, in other media, namely, Teflon was selected and slightly less amount of adsorption onto Teflon was observed. This depicts that material from which the system was composed of is an important factor to consider during the hydrophobic organic compounds, like TCS, removal from water.

Although nanofiltration removal efficiency for TCS from water was reported above 90% in the literature, this study did put forward that it is not the realistic figure to report on the removal efficiency of TCS by nanofiltration. As evidenced from the results obtained from this study, the real TCS removal efficiency of nanofiltration is much less, due to the adsorption of TCS by the system's inner surfaces, as well. In this respect, however it should be considered that, in real treatment plants due to saturation of the system and membrane in first hours of start-up, similar result could not be obtained. Hence, treatment efficiency would differ. However one should be aware of this fact when performing a lab-scale membrane treatability study with hydrophobic compounds like TCS.

Moreover, one important conclusion that could be drawn from our study is that HA level of the feed water is one of the important factor to consider, when the concern is the removal of TCS from raw water sources by nanofiltration. The greater the HA content the greater the TCS removal efficiency is.

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APPENDIX A

RESULTS FOR EXPERIMENT SETS

1. Experimental Data for Set 1 with DL-NF membrane at 6.9 bar TMP, and CFV: 1.2 m/s.

Table A-1 Clean Water Flux vs. Time

	Time(h)	Flux ($L/m^2.h$)
T0	0	45.0
T1	2	44.0
T2	5	43.6
T3	7	42.9
T4	8	45.1
T5	9	46.1
T6	10	46.1

Table A-2 Raw Water Flux vs. Time

	Time (h)	Flux ($L/m^2.h$)
T0	0	41.1
T1	1	40.9
T2	2	40.1
T3	3	39.3
T4	6	38.7
T5	8	38.7

Table A-3 Clean Water Flux vs. Time

	Time (h)	Flux (L/m^2.h)
T0	0	41.3
T1	1	47.8
T2	5	45.9
T3	7	45.9
T4	8	45.9

Table A-4 Clean Water Flux After Cleaning vs. Time

	Time (h)	Flux (L/m^2.h)
T0	0	41.3
T1	1	43.6
T2	4	46.7
T3	6	49.5
T4	8	49.5

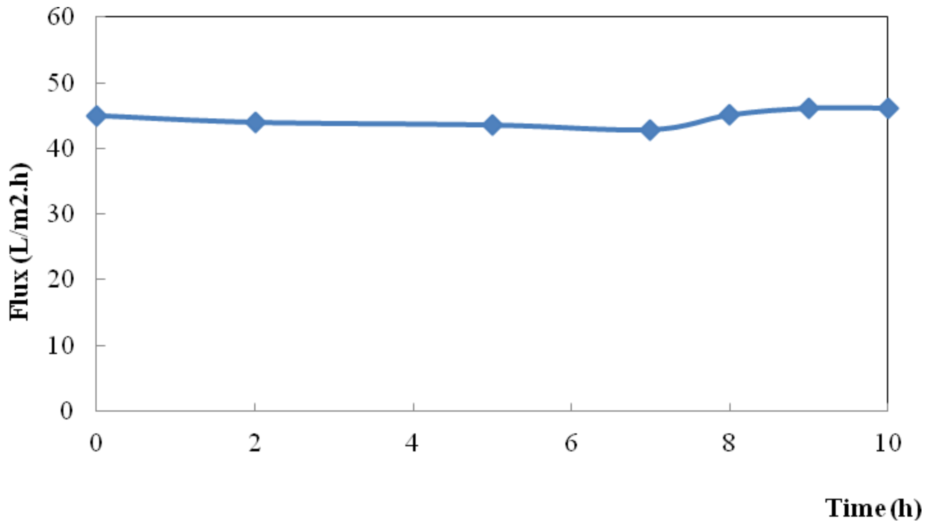

Figure A-1 Clean water Flux vs. Time

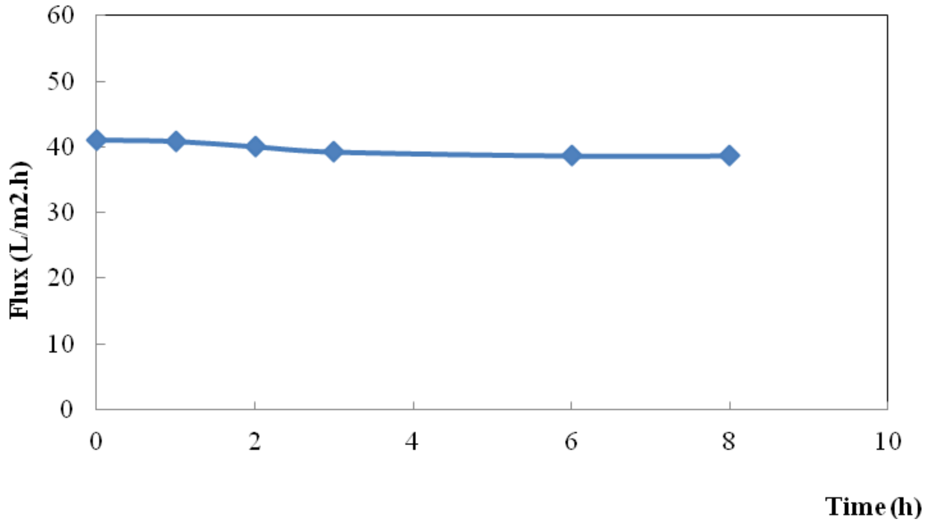

Figure A-2 Raw Water Flux

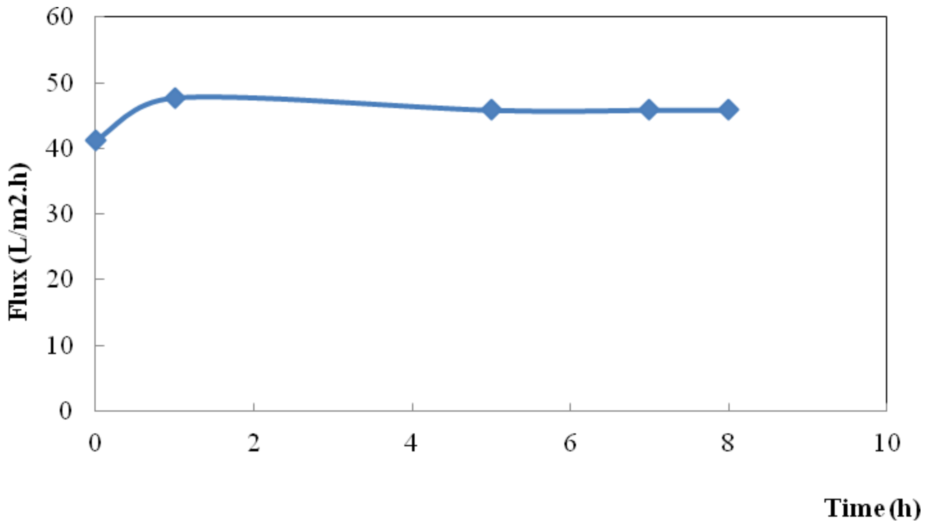

Figure A-3 Clean Water Flux vs. Time before cleaning

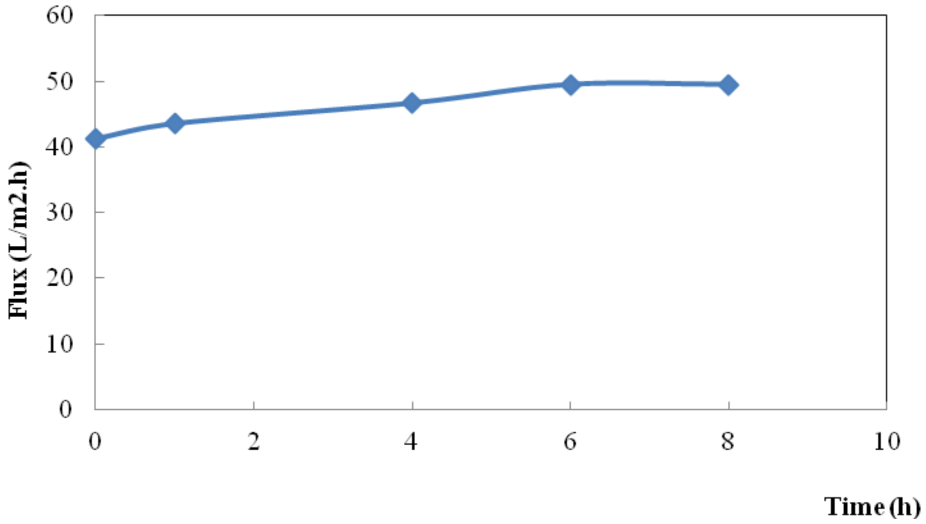

Figure A-4 Clean Water Flux After Cleaning vs. Time

2. Experimental Data for Set 2 without membrane in the system (TMP and CFV: Not applicable)

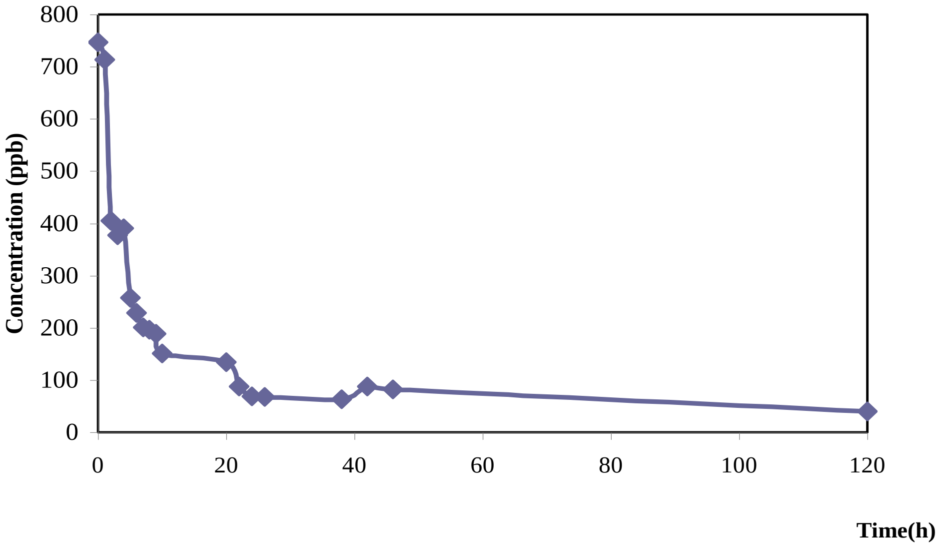

Figure A-5 TCS Change in Feed Tank of filtration Set-up, without membrane (Set 2)(C_0=750 ppb)

3. Experimental Data for Set 3 without membrane in the system (TMP and CFV: Not applicable)

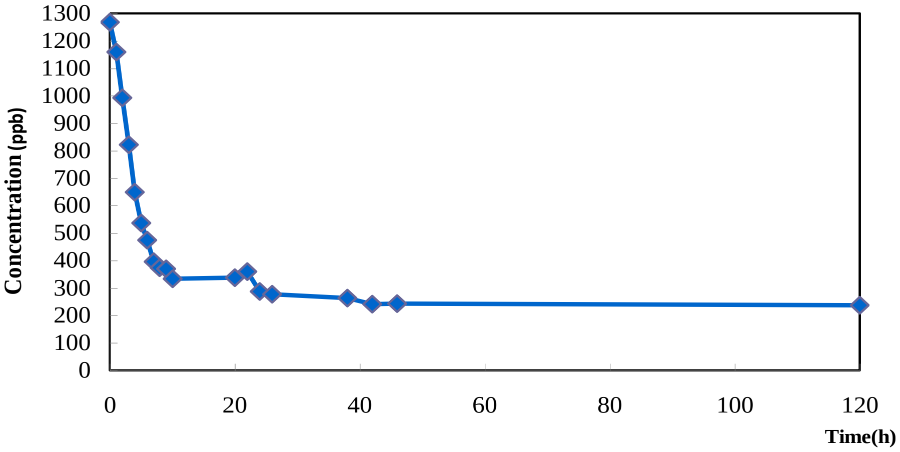

Figure A-6 TCS Change in Feed Tank of filtration Set-up, without membrane (Set 3)(C_0=1250 ppb)

4. Experimental Data for Set 4 Set with DK-NF membrane at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity. C_0=5000ppb, (Uncompacted Membrane)

Table A-5 Clean Water Flux

	Time (h)	Flux L/m^2.h)
T0	0	53.1
T1	2	52.5
T2	4	53.6
T3	6	53.6

Table A-6 Raw water Flux (C0=5000ppb TCS)

	Time (h)	Flux ($L/m^2.h$)
T0	0	43.6
T1	2	44.8
T2	4	38.7
T3	20	44.5
T4	23	45.1
T5	40	44.8
T6	41	43.0
T7	44	43.0
T8	46	43.0

Table A-7 Clean Water Flux Before Cleaning

	Time (h)	Flux ($L/m^2.h$)
T0	0	51.8
T1	2	50.8
T2	4	51.2
T3	8	51.2
T4	10	51.2

Table A-8 Clean water flux after cleaning

	Time (h)	Flux (L/m^2.h)
T0	0	49.6
T1	2	49.5
T2	4	48.7
T3	6	48.7
T4	8	48.7

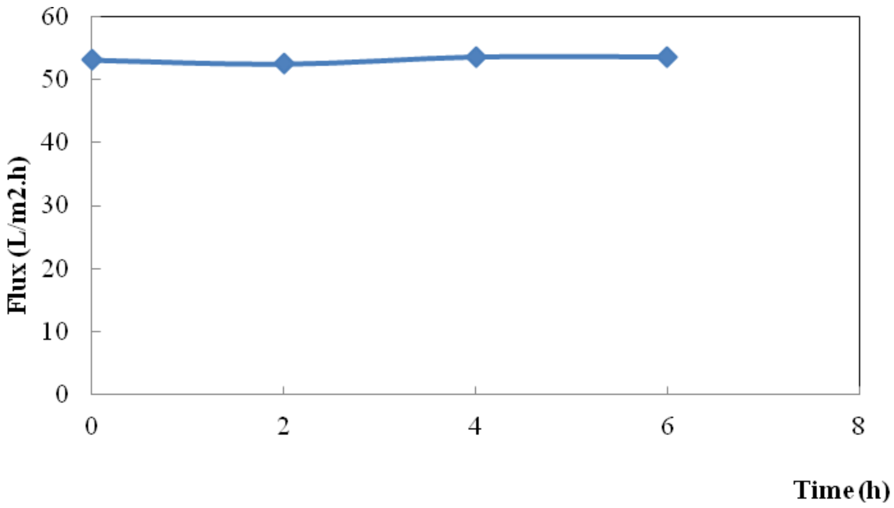

Figure A-7 Clean Water Flux

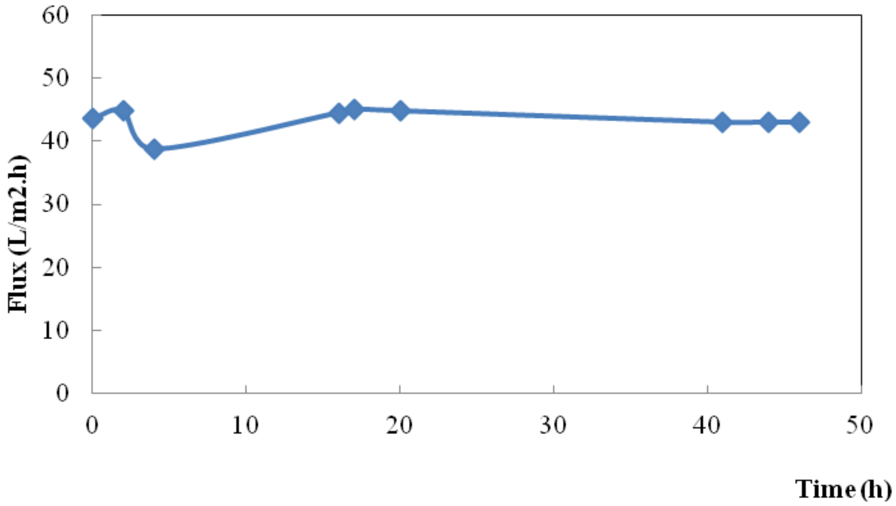

Figure A-8 Raw water Flux (C0=5000ppb TCS)

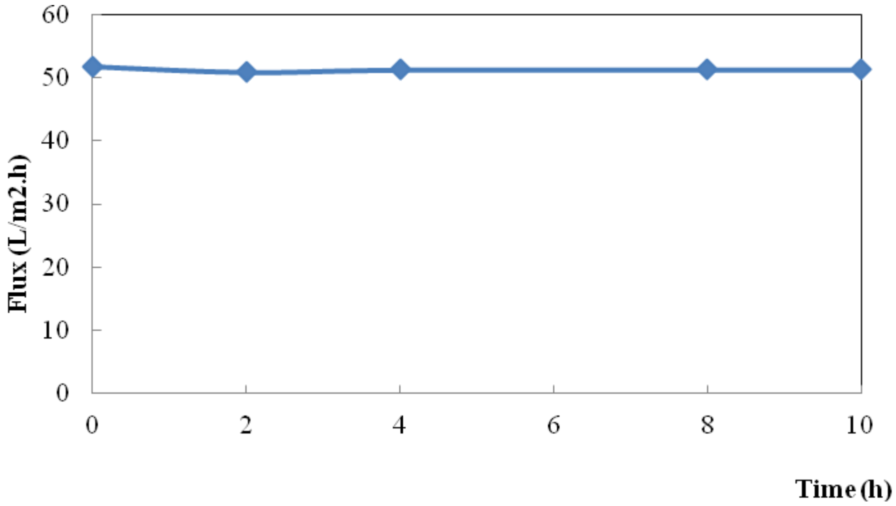

Figure A-9 Clean Water Flux Before Cleaning

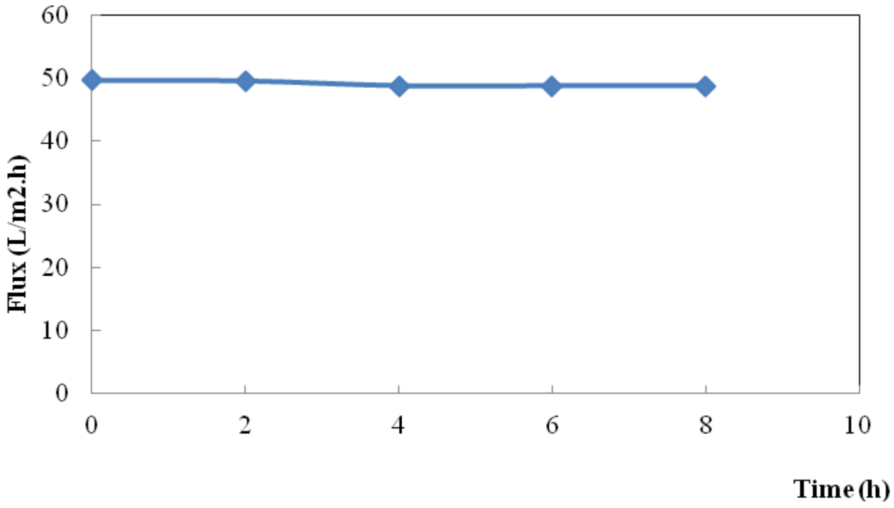

Figure A-10 Clean water flux after cleaning

5. Experimental Data for Set 5 with DK-NF membrane at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity. C_0=2500ppb, With Humic Acid 10 mg/L

Table A-9 Clean water flux

	Time (h)	Flux (L/m^2.h)
T0	0	38.4
T1	2	38.0
T2	4	37.8
T3	6	36.0
T4	10	36.0

Table A-10 Raw water Flux (C_0=2500ppb TCS)

	Time (h)	Flux ($L/m^2.h$)
T0	0	29.0
T1	2	28.4
T2	6	28.0
T3	10	28.5
T4	23	28.3
T5	25	28.3
T6	30	28.3

Table A-11 Clean water flux before cleaning

	Time (h)	Flux ($L/m^2.h$)
T0	0	32.2
T1	2	32.5
T2	4	33.0
T3	20	36.4
T4	22	36.4
T5	26	36.4

Table A-12 Clean water flux after cleaning

	Time (h)	Flux ($L/m^2.h$)
T0	0	36.9
T1	2	40.2
T2	4	40.2
T3	6	40.1
T4	8	40.2

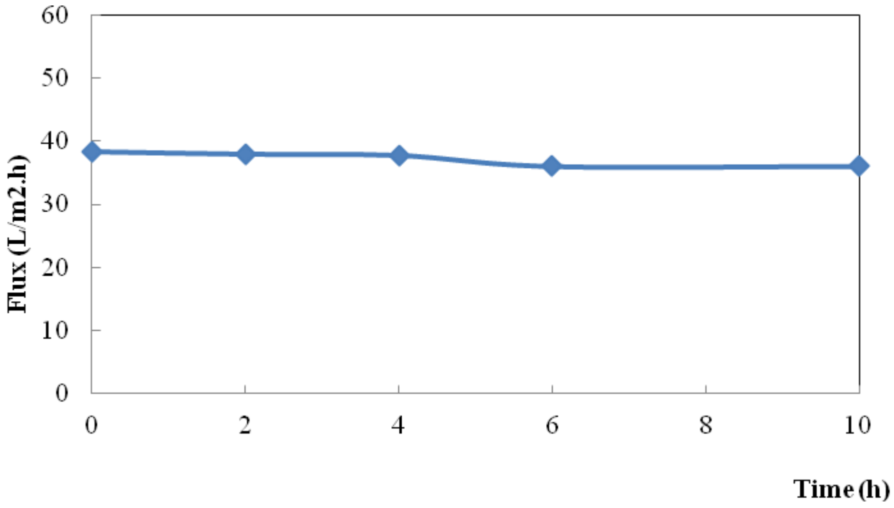

Figure A-11 Clean Water Flux

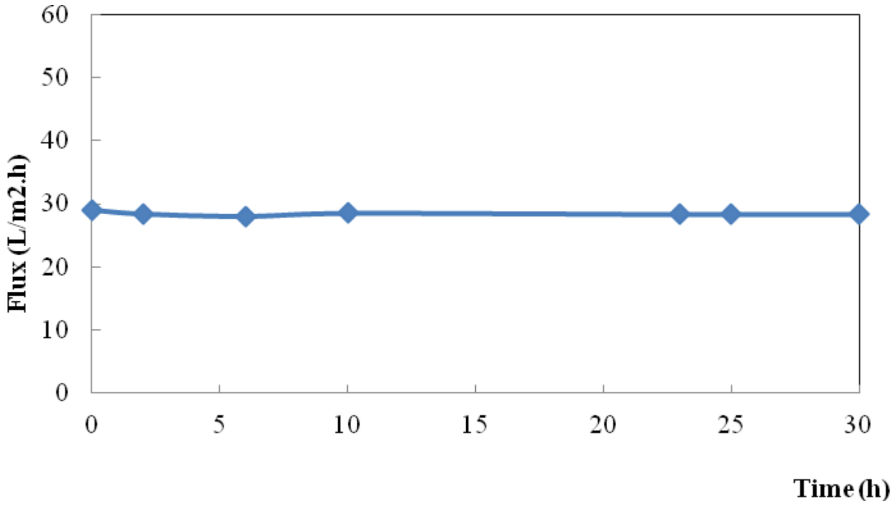

Figure A-12 Raw water Flux (C_0=2500ppb TCS)

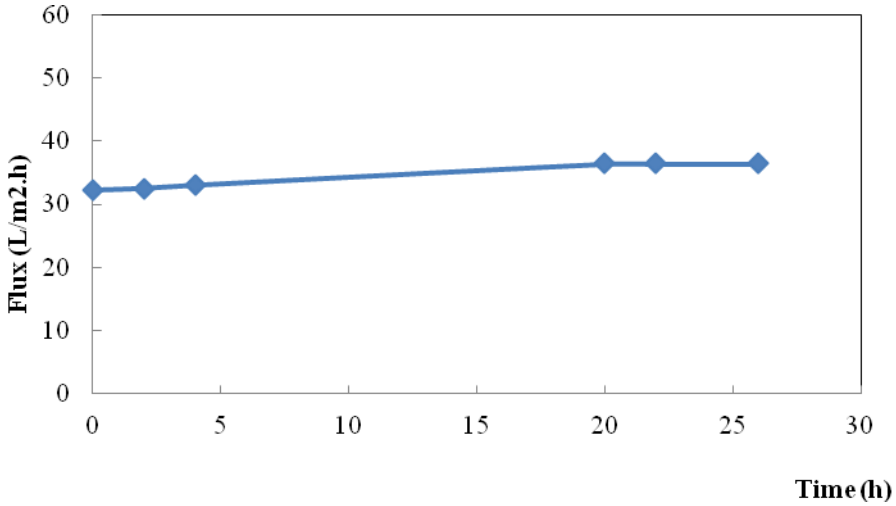

Figure A-13 Clean water flux Before cleaning

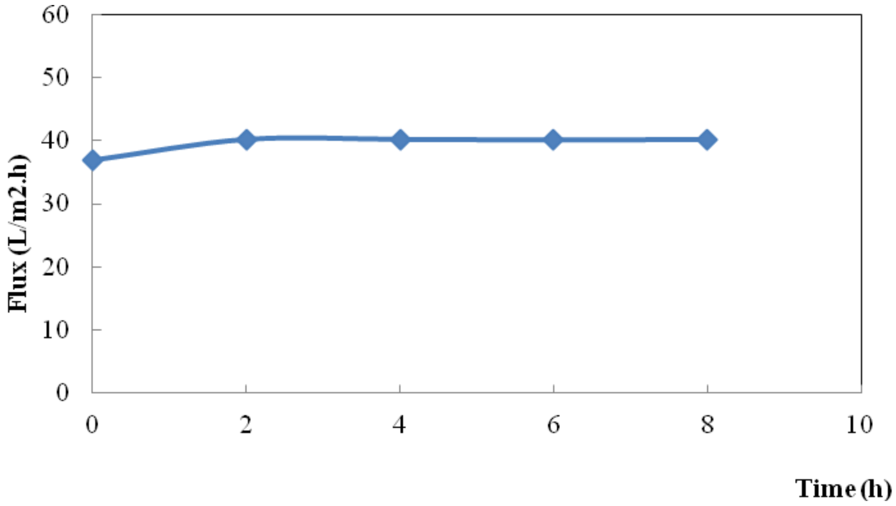

Figure A-14 Clean water flux after cleaning

6. Experimental Data for Set 6 DK-NF membrane at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity. C_0=5000ppb, With Humic Acid 10 mg/L

Table A-13 Clean water flux

	Time (h)	Flux (L/m^2.h)
T0	0	39.8
T1	2	40.6
T2	4	41.5
T3	6	41.1
T4	20	40.8
T5	21	40.8

Table A-14 Raw water Flux (C_0=5000ppb TCS) (@t=33h Humic Acid added to feed tank)

	Time (h)	Flux (L/m^2.h)
T1	0	49.5
T2	2	48.5
T3	4	41.9
T4	23	41.5
T5	25	41.2
T6	30	40.2
T7	33	40.2
T8	36	40.2
T9	56	40.2

(Humic acid addition did not change the flux value which is 40.2 L/m^2.h)

Table A-15 Clean water flux before cleaning

	Time (h)	Flux (L/m^2.h)
T0	0	35.0
T1	2	37.6
T2	4	36.6
T3	20	42.4
T4	24	42.6
T5	26	42.6

Table A-16 Clean water flux after cleaning

	Time (h)	Flux (L/m^2.h)
T0	0	48.5
T1	2	47.6
T2	6	49.5
T3	8	47.1
T4	10	47.1

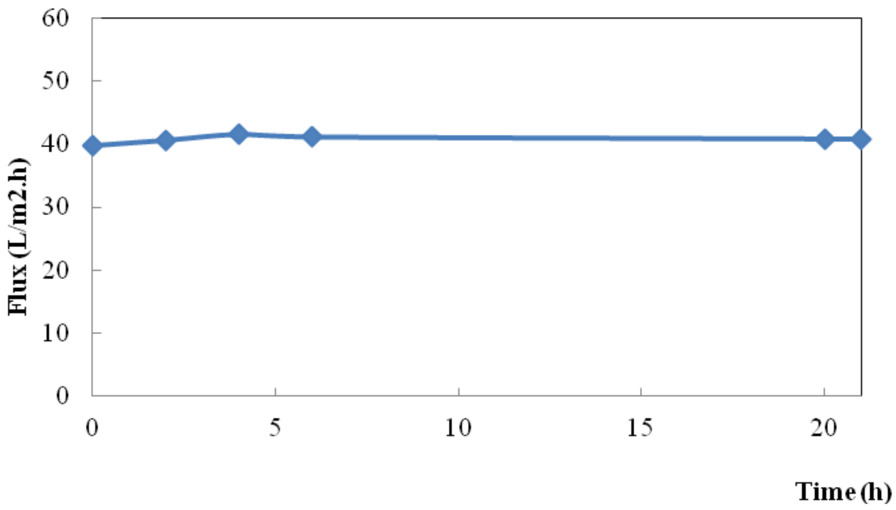

Figure A-15 Clean water flux

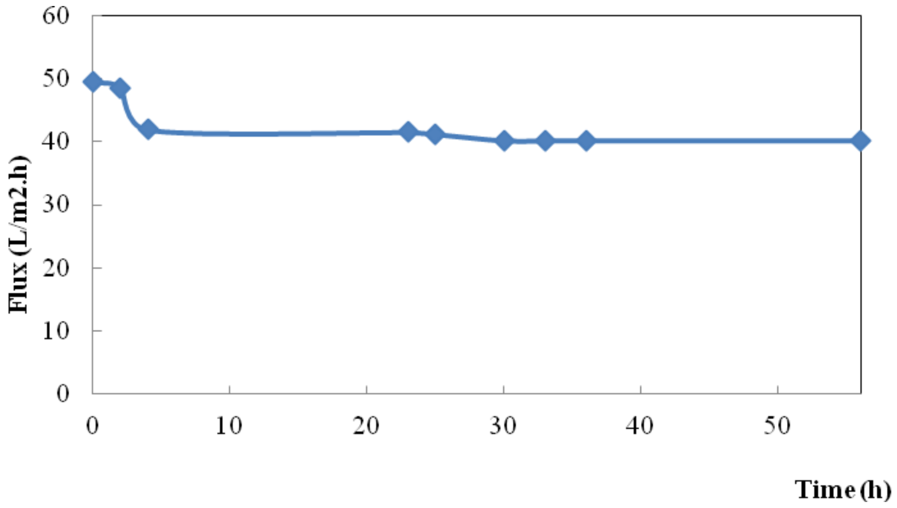

Figure A-16 Raw water Flux (C_0=5000ppb TCS) (@t=33h HA added to feed tank)

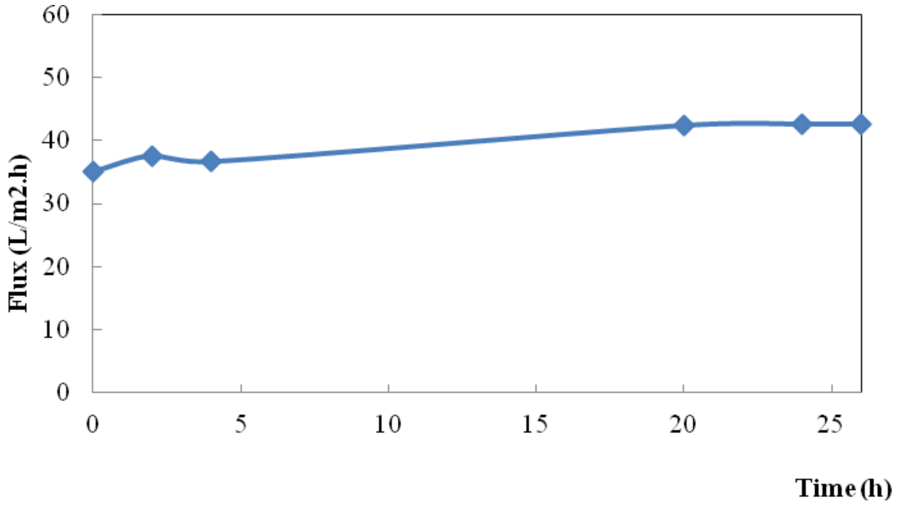

Figure A-17 Clean water flux before cleaning

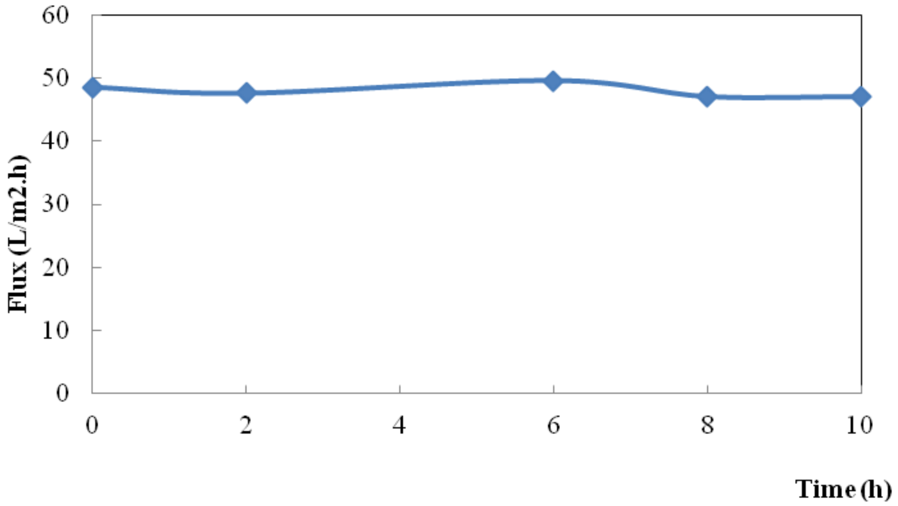

Figure A-18 Clean water flux after cleaning

7. Experimental Data for The Set 7 with DK-NF membrane at 6.9 bar transmembrane pressure, 1.2 m/s cross-flow velocity. C_0=5000ppb, With Humic Acid 26 mg/L

Table A-17 Clean Water Flux

	Time (h)	Flux (L/m^2.h)
T0	0	54.2
T1	2	61.2
T2	4	60.9
T3	6	61.8
T4	20	58.2
T5	21	58.2

Table A-18 Raw Water Flux (C_0=5000ppb TCS) (@t=30h HA added to feed tank)

	Time (h)	Flux (L/m^2.h)
T1	0	57.1
T2	2	56.6
T3	4	55.9
T4	21	55.4
T5	27	55.4
T6	30	55.4
T7	31	55.4
T8	54	53.1
T9	55	52.1
T10	66	51.4
T11	68	50.4
T12	76	46.9
T13	78	46.9

Table A-19 Clean Water Flux Before Cleaning

	Time (h)	Flux (L/m^2.h)
T0	0	37.3
T1	2	37.2
T2	4	39.0
T3	20	50.4
T4	24	55.9
T5	28	55.9

Table A-20 Clean Water Flux After Cleaning

	Time (h)	Flux (L/m^2.h)
T0	0	60.1
T1	2	60.6
T2	6	57.4
T3	8	57.8
T4	10	57.8

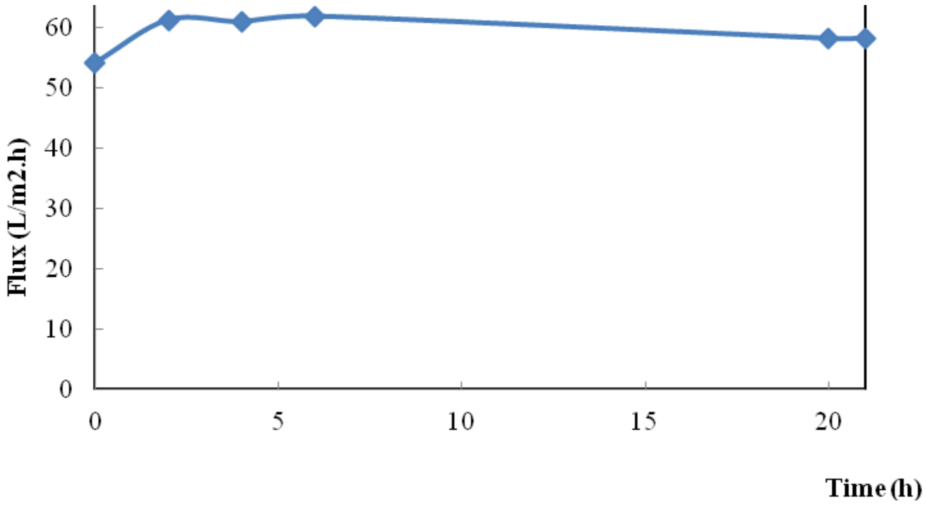

Figure A-19 Clean Water Flux

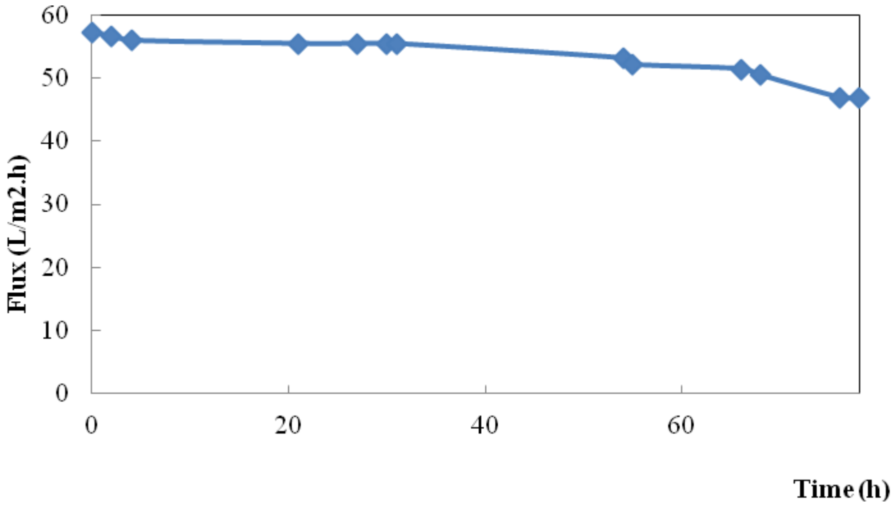

Figure A-20 Raw Water Flux

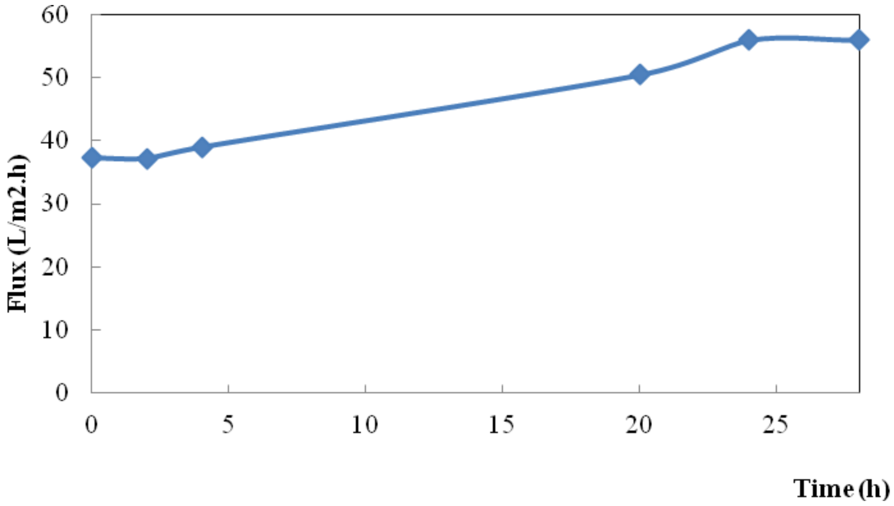

Figure A-21 Clean Water Flux Before Cleaning

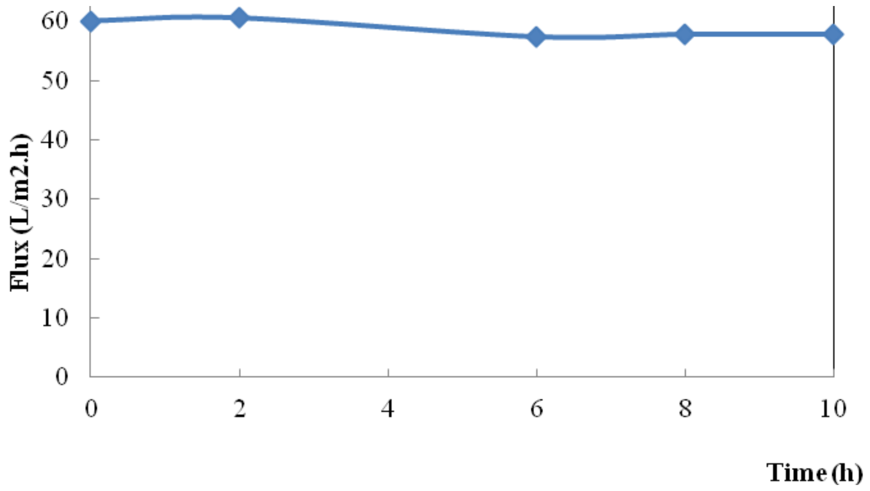

Figure A-22 Clean Water Flux After Cleaning

8. TOC Measurement Calibration Graph

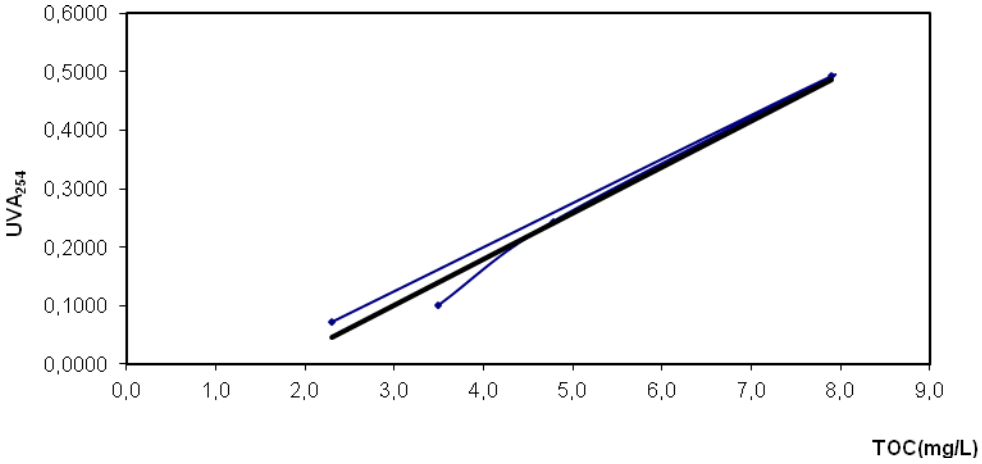

Figure A-23 UVA$_{254}$ calibration for TOC Measurement

Equation for UVA$_{254}$ calibration for TOC Measurement: $y = 0.087x – 0.1903$ and $R^2 = 0.9934$

Table A-23 UVA_{254} calibration for TOC Measurement

Average TOC	UVA_{254}	UVA_{254}	Average UVA_{254}
2.3	0.0723	0.0721	0.0722
3.5	0.1012	0.1011	0.1012
4.8	0.2438	0.2444	0.2441
7.9	0.4923	0.4921	0.4922