

## INVESTIGATING REMOVAL OF PESTICIDES FROM WATER BY NANOFILTRATION MEMBRANE TECHNOLOGY

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### **Abstract**

Agricultural activities form the backbone of Kenya's economy. In order to control crop losses, pesticides are used and in the recent past, more of the pesticides have been used to increase production. However, the effect of pesticides on the environment is very complex as undesirable transfers occur continually among different environmental sections. This eventually leads to contamination of drinking water sources such as rivers and lakes located near active agriculture areas, including flower farms around Lake Naivasha where poisoning of lake water by pesticides caused fish deaths. The aim of this paper was to investigate application of nanofiltration membrane technology in the removal of pesticides from water. A pesticide, atrazine was selected for the study due to its extensive use in controlling weeds and the adverse environmental effects associated with it. Membrane filtration was used using a laboratory scale crossflow filtration units that operated in total recycle mode to ensure even concentration of atrazine in the feed solution to separate atrazine from water. Concentration of atrazine in aqueous solution was analyzed using high performance liquid chromatography (HPLC). Retention of atrazine by four nanofiltration membranes i. e. NF90, NTR7250, and NF270 was investigated. The effect of feed solution pH, concentration and feed pressure were investigated, as was the effect of humic substances and titanium dioxide catalyst on retention by membranes. pH and feed pressure showed influence on retention of atrazine while initial feed concentration had little influence. The presence of HA led to improved atrazine rejection efficiency but led to flux decline on all membrane tested while TiO<sub>2</sub> led to high rejection efficiency and low flux decline. Of all four membranes, NF90 showed the best performance in retention of atrazine in water while NTR7250 showed the least. This indicated that with proper membrane selection, it's possible to treat water contaminated with pesticides to acceptable levels.

**Key words:** Pesticides, nanofiltration, membranes, retention

## 1.0 Introduction

Agricultural activities are the main food source for the world's population. Pesticides are used in order to control crop losses and in the past years, more and more pesticides have been used to increase production. However, the effect of pesticides on the environment is very complex as undesirable effects occur to both human, animals and the aquatic environment. They lead to contamination of drinking water sources such as rivers, lakes and groundwater.

In recent years various international and local regulations have become stricter concerning the amounts of pollutants in wastewaters and the quality of the treated effluents discharged into the aquatic environment. This is mainly because the pollutants are known or suspected to cause harmful ecological effects. Widespread concerns are being raised due to the increasing number of cases, when such contaminants are detected in surface water bodies and due to their potential to affect the development, reproduction and health of wildlife, livestock and even humans. Most contaminants found in aquatic environment mainly comprise of organic compounds. Organic matter found in water spans a wide spectrum, with molecular weights ranging from several thousands to less than 100 g/mol.

Most compounds on the upper end of this spectrum are of natural origin, and they are commonly known as natural organic matter (NOM). Trace organics are generally located at the lower end of the organic compound spectrum. The trace organics include pesticides, trihalomethanes (THMs), polychlorinated biphenols (PCBs) and polyaromatic hydrocarbons (PAHs) and are commonly referred as persistent polar pollutants (PPPs) due to their persistence in the environment. PPPs have been identified as an increasing problem in our drinking water supplies. Such substances can enter the water supply from various sources and are not effectively removed by conventional water treatment processes.

Pesticides have been classified as PPPs due to their resistance to natural degradation processes, and hence their ability to remain in the environment for long periods of time. By their very nature, they are designed to be toxic and kill unwanted organisms, but can attack non-target organisms and as a result cause serious environmental damage. Due to the extensive use of pesticides in industry and agriculture, many water sources are contaminated with pesticides, especially, wastewater from agriculture farms and pesticides formulating or manufacturing plants (Shaalan *et al.*, 2007).

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has been a widely used herbicide to control certain annual broadleaf weeds and grasses throughout the world over the last 50 years. It has been found in groundwater at concentrations exceeding the ground and drinking water limit of  $0.1 \mu\text{g L}^{-1}$  of the European Union (Spliid and Koppen, 1998). It is less expensive and persists longer in the soil than alternative herbicides, with a lifetime of days or even years in the environment.

Conventional water treatment processes, specifically coagulation–flocculation, sedimentation and conventional filtration, are not very effective in removing pesticides from drinking water (Plakas *et al.*, 2006). Traditional plants are far from efficient and offer removal levels that rarely exceed 10–20% for atrazine and 40% for simazine (Zhang *et al.*, 2004). Disinfection and water softening, however, may lead to pesticide transformation and formation of disinfection byproducts (USEPA, 2001). Removal of pesticides for the production of drinking water can be conducted by activated carbon filtration (Herrera *et al.*, 2006, Acero *et al.*, 2009). It is an expensive procedure that requires frequent regeneration. This is because organic micropollutants, such as pesticides, may be present at the  $\mu\text{g/L}$  level. NOM concentrations may be 10,000 times higher, hence the adsorption columns have to be regenerated rapidly, because the column capacity is mainly used for NOM adsorption instead of pesticides adsorption (Bruggen *et al.*, 2003). In parallel, some chemical treatments have been applied for the reclamation and reuse of different wastewaters and surface waters containing pesticides, by using clean-up chemicals and techniques such as several oxidants like ozone and hydrogen peroxide, UV radiation, and their combinations (advanced oxidation processes) (Ormad *et al.*, 2008, Acero *et al.*, 2009). The reaction may not be very selective for degradation, as is the case in oxidation process, where ozone is known to produce a variety of aldehydes (Nghiem, 2005).

Over the past few years, nanofiltration (NF) membranes have been studied as potentially useful means of pesticide removal considering the fact that the molecular weights (MWt) of most pesticides are more than 200 Da (Kamrin *et al.*, 1997, Plakas *et al.*, 2006). Nanofiltration has been successfully applied in drinking water treatment plant in Mery-sur-Oise, France (Cyna *et al.*, 2002) and Heemskerk (Hofman *et al.*, 1997) Holland as

well as Saffron Walden in England. However, there is still a long list of pesticides in guidelines for drinking water by World Health Organization (WHO, 2004) but there is lack of adequate data for their effective separation using membranes. Therefore, there is still room for investigation of the feasibility of using membrane technology to completely remove atrazine from water.

The main objective of this study was to investigate the removal of atrazine by NF membranes. The effect of operating parameters of the feed solution on the rejection efficiency for atrazine; pH, concentration and feed pressure were investigated. The effect of humic substances and titanium catalyst on the rejection efficiency and operation of the membranes was of concern too.

## 2.0 Materials and Methods

### 2.1 Experimental Procedure

The experiment was conducted to investigate the retention of atrazine by three NF membranes. The effect of solution pH on retention of atrazine by the membranes was assessed. Three different pH values for the feed solution were used namely; pH 4, pH 7 and pH 9. Furthermore, the effect of humic acid and titanium dioxide on the membrane performance was studied.

### 2.2 Membranes

Previous researches have shown that membrane processes, such as reverse osmosis (RO) and nanofiltration (NF) are considered promising candidates for the removal of low molar mass organic compounds of environmental concern, like pesticides (Plakas and Kalabelas, 2009, Shaalan *et al.*, 2007). The molar masses of most pesticides and herbicides are in the range of 200-400 g/mol, which is the normal cut-off range for most NF membranes. Three NF membranes were investigated in this study. The characteristics of the membrane used are shown in Table 1.

Table 1: Characteristics of membranes used in the study

	NF270	NF90	NTR7250
Manufacturer	Dow (Filmtec)	Dow (Filmtec)	Nitto Denko, Japan
MWCO	200 <sup>a</sup>	200 <sup>a</sup>	300-450 <sup>b</sup>
Zeta potential (mV)	-21.6 <sup>c</sup>	-24.9 <sup>c</sup>	-6 <sup>d</sup>
Contact angle	28±2 <sup>e</sup>	62±2 <sup>e</sup>	Na <sup>f</sup>
Membrane pore size (nm)	0.71±0.14 <sup>g</sup>	0.55±0.13 <sup>g</sup>	0.65 <sup>a</sup>
NaCl retention (%)	66.4 <sup>h</sup>	99.5 <sup>h</sup>	50 <sup>i</sup>
Membrane material (skin)	Polyamide <sup>j</sup>	Polyamide <sup>j</sup>	Polyvinyl alcohol <sup>k</sup>
pH range	3-10 <sup>j</sup>	3-10 <sup>j</sup>	2-9 <sup>k</sup>
Maximum temperature	45 <sup>j</sup>	45 <sup>j</sup>	40 <sup>k</sup>

a- As stated by manufacturer

b- Verliefde, *et al*, 2005

c- Plakas and Kabelas, 2008; Measured at pH7 and 30\_S/cmKCl solution (PAAREKA-Electro Kinetic Analyzer RV. 4.0).

d- Nymston *et al.*, 1995; Measured at pH7 and salt solution used; 1.0 mM KCl, T= 25°C, p = 0-70 cm H2O.

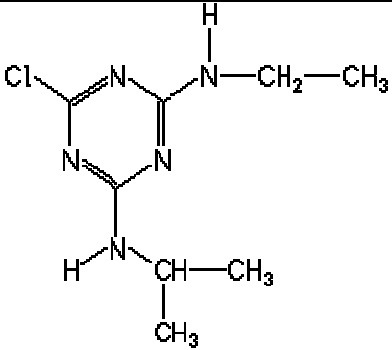
e- Plakas and Kabelas, 2008; Sessile drop contact angle measurements.

f- na (not available)

### 2.3 Herbicide

The herbicide atrazine which has had a significant share of the herbicide market and is detected with great frequency in drinking water sources, was selected for the experiments. The molecular structure and some physicochemical properties of the tested herbicide is presented in Table 2. The herbicide is hydrophobic (log Kow > 2), moderately soluble in water and therefore weakly polar compound (Plakas and Kalabelas, 2008).

Table 2: Properties of herbicide used in the study (W. S. S. A., 1994)

Chemical structure	
Molecular formula	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>
Molar mass (g/mol)	215.69
Molecular size (nm) <sup>a</sup>	0.788
Log K <sub>ow</sub>	2.68
Aqueous solubility (mg/L)	33

a- Bruggen et al., 1998

#### 2.4 Solution Preparation

A standard stock solution of concentration 100 mg/L was prepared for atrazine in high-performance liquid chromatography (HPLC)-grade methanol and stored at 4 °C. The feed atrazine solutions at a level of 10 mg/L and 20 mg/L were prepared from stock solutions by diluting with pure water. The experiments were carried out with feed solutions at pH 4, pH 7, pH 10 and natural pH of atrazine solution which is pH 8.3.

The pH of the atrazine feed solution was adjusted to different pH by adding 1M NaOH or 37% (w/w) HCl (Fisher Scientific, Pittsburg, PA). The pH measurement was conducted using pH meter (Mettler Toledo Delta 320 pH Meter). Methanol was used for preparation of stock solution but the cosolvent effect was not considered in this paper.

Retention of 10 ppm atrazine solution was tested in presence of humic substances and TiO<sub>2</sub>. Humic acid (HA) was used to simulate the effect of organic matter found in natural water on the atrazine retention. Since humic substances concentrations in natural waters usually fall in the range of 2–40 mg/L (Jones *et al.*, 1998) the solution was prepared with ultra-pure water and with a concentration of 10 mg/L humic acid. The HA was obtained in powder form and used without further purification. Humic acid sodium salts was supplied by Sigma–Aldrich company. Titanium dioxide solution (10 ppm TiO<sub>2</sub>, C380 from TIPE Company, China) had primary particle size of 6–8 nm.

#### 2.5 Filtration Setup

The filtration was carried out in a laboratory scale cross-flow filtration unit that operated in total recycle mode where permeate and retentate were returned to the feed tank. A schematic presentation of the unit is shown in Figure 1 below. The model solution in the feed tank was pumped to flat sheet membrane module by a centrifugal pump. The unit consisted of three membrane modules arranged in parallel. The required pressure and flow velocity were achieved by controlling the power of the pump and the back pressure valve after the membrane module. The effective surface area of each membrane module was 10.4 cm<sup>2</sup>. The temperature was maintained constant by re-circulating cold water in the jacket around the feed tank.

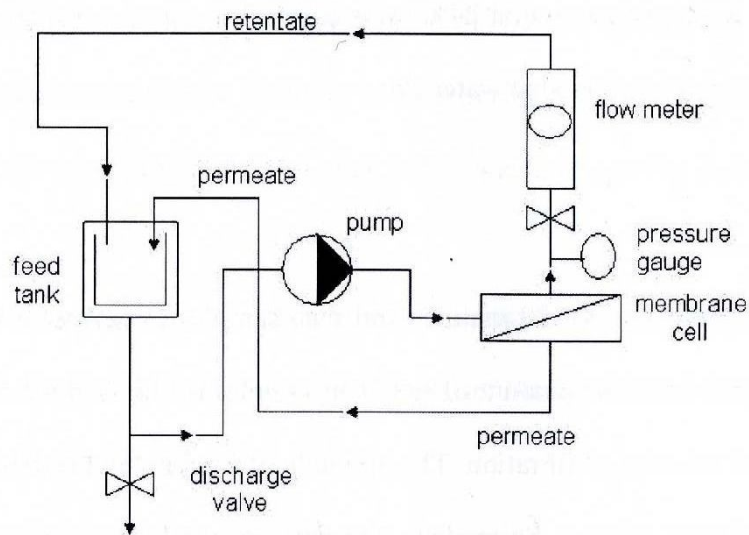


Figure 1: Schematic diagram of cross flow filtration unit

## 2.6 Filtration Procedure

The feed tank capacity 5 L was filled with the feed solution. Prior to commencement of experiment, the pure water flux was measured. The filtration experiments were carried out at pressures of 6 bar and 12 bar respectively and a velocity of 2.5 m/s and temperature of 25°C.

The filtration protocol involved a sequence of the following steps

- (i) First, the membrane was rinsed with tap water for several minutes and afterwards it was fitted in the module, then the membrane sample was pressurised with pure water under 15 bar for 4 hours to ensure that the removal of preservatives from the new membrane coupon was complete and that it was compacted (Plakas et al. 2008). Compaction is crucial in every membrane filtration protocol as it may change both the active layer and its support, thus affecting the flux and the rejection properties of the membrane. To eliminate this impact, membranes were subjected to a higher pressure (15 bar) than the operating pressure (12 bar, maximum for this study) to ensure flux stability during experiments (Schafer et al., 2005).
- (ii) Measurement of the pure water flux at 6 bar, then stabilized water flux at different operating pressures was obtained and membrane permeability value ( $L_p$ ) was determined from the slope of flux against pressure graph.
- (iii) Filtration of 10 ppm atrazine at 6 bar and 12 bar, each for 3.5 hours respectively at natural pH (8.3) of the solution.
- (iv) Filtration of 20 ppm atrazine at 6 bar and 12 bar, each for 3.5 hours respectively at natural pH of the solution.
- (v) Filtration of 10 ppm atrazine solution at pH of 4, 7 and 10 respectively each for a duration of 3.5 hours and pressure 12 bar.
- (vi) Filtration of 10 ppm atrazine solution in presence of 10 mg/L  $TiO_2$  catalyst and 10 mg/L HA solution respectively at a pressure of 12 bar.

After each experiment, the membranes were rinsed with pure water at same conditions as the filtration process and pure water flux measurements were made. Permeate from the bottom of the membrane modules was collected on 30 minute interval and its mass was measured. The cumulative mass was converted to cumulative permeate volume ( $V_p$ ), and the permeate flux ( $J_w$  for pure water, or  $J_v$  for the atrazine solutions) was obtained by means of Equation 1:

$$J_w \text{ or } J_v = \frac{\Delta V_p}{\Delta t \cdot A} \dots \dots \dots (1)$$

Where  $\Delta V_p$  is the accumulated permeate mass during the time difference  $\Delta t$  and  $A$  is the membrane area. At the same time, samples were collected for analysis of atrazine concentration by use of HPLC.

### 2.7 Analytical Method

The concentration of atrazine in feed and permeate was analysed using a HP 1050 high performance liquid chromatography (HPLC) by on-line coupled with a DAD detector and a ESI-MS by Agilent (Germany). Isocratic eluent: 20 mM ammonium hydroxide-methanol mixture (50:50, v/v). flow rate: 0.15 mL/min. Column: Luna 3u C18(2) 100A reversed phase (100 mm x 2.00 mm, 3  $\mu$ m particles) by Phenomenex (Copenhagen, Denmark). Separation temperature was ambient (app. 27 °C). The samples were injected with auto-sampler. The volume of the sample in each injection was 2  $\mu$ l.

The effectiveness of a membrane is measured on how much of the feed material is retained during operation. This is termed as retention and is calculated using the following equation:

$$R = \left(1 - \frac{cp}{cf}\right) * 100 \dots\dots\dots (2)$$

where  $R$  is the observed retention,  $cf$  the concentration of the feed and  $cp$  the concentration of the permeate.

## 3.0 Results and Discussion

### 3.1 Influence of pH, Atrazine Concentration and Pressure on Retention

The retention performance of atrazine by NF90, NTR7250, NF270 membranes at different pressure, concentration and pH is presented in Figure 3.

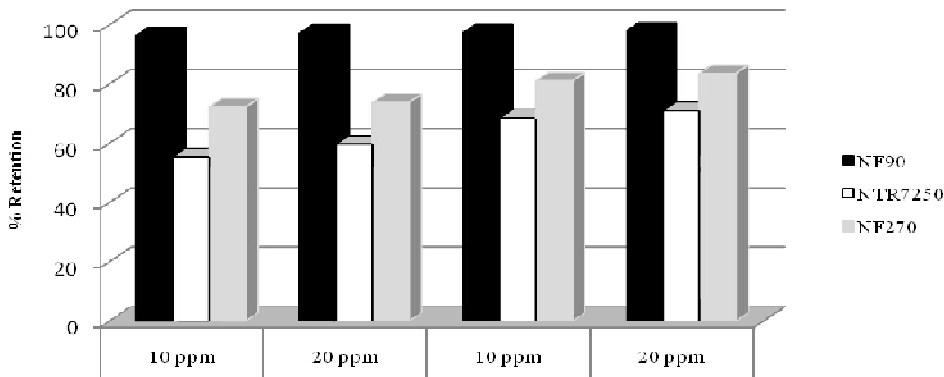


Figure 3: Membrane retention performance at a flow velocity of 2.5 m/s, Temp. 25°C and pH 8.3

From these figures, it is obvious that the retention of atrazine tended to be better when the pressure was increased from 6 bar to 12 bar. It can be seen that NF90 produced the best retention for atrazine being more than 95% at the operating pressure and feed concentration tested. The performance of NF270 was the second highest of all three membranes tested while NTR7250 showed lower retention than NF270 when both were operated at the same pressure and feed concentration. Higher retention was observed at higher pressure due to the increased water flux that caused dilution of permeate from the membranes. Similar findings were reported by Armad *et al.*, (2008) during filtration of dimethoate and atrazine using nanofiltration membranes at different pressures.

As Figure 3 shows the retention did not vary greatly regardless of the initial atrazine concentration. The retention results with atrazine solutions are in agreement with observations made by other researchers (Zhang *et al.*, 2004, Plakas *et al.*, 2009) in that herbicide concentration does not significantly affect their retention. In practical terms, the consequence of this result is that different stages of a nanofiltration plant have the same efficiency level so far as atrazine is concerned at very dilute concentration. The influence of the pH on the retention is shown in Figure 4.

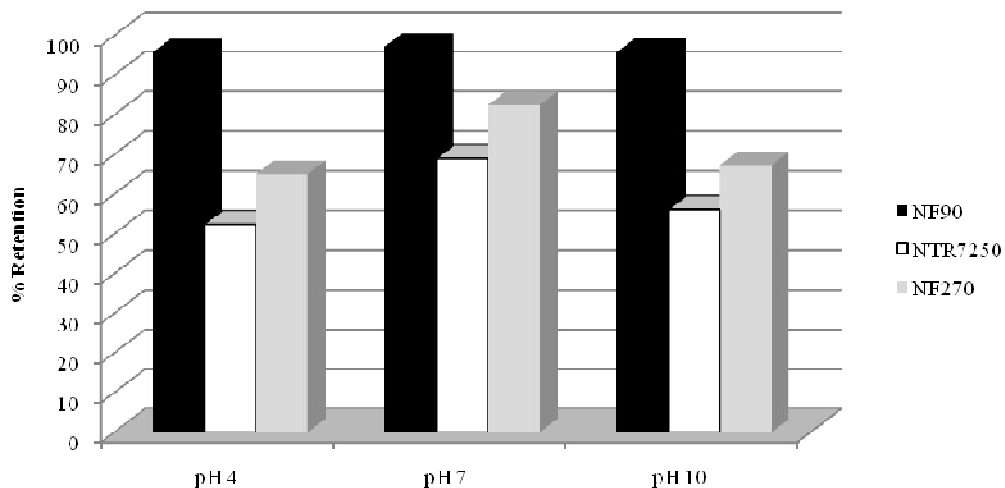


Figure 4: Membranes retention performance at various pH conditions; Temp. 25<sup>o</sup>C, crossflow velocity 2.5 m/s, pressure of 12 bar for 10 ppm atrazine concentration

NF90 membrane showed almost consistent retention for all tested conditions while the NF270 and NTR7250 showed varying retention at different pH. The retention was the highest at pH 7; while at pHs 4 and 10, the retentions were consistently lower. This was caused by ion adsorption: at higher pH, OH<sup>-</sup> ions can adsorb on membrane surface, resulting in an increase of the membrane charge. Polar components such as pesticides have a lower rejection when the membrane charge increases, because they are dipoles which can have a preferential orientation towards the membrane in the sense that the side of the dipole with a charge opposite to the membrane charge is the closest to the membrane. In this way, the preferential orientation results in an increased attraction, an increased permeation and thus a lower rejection. At lower pH, the same effect might occur with H<sup>+</sup> ions. The NF90 and NF270 have the same MWCO as seen on Table 1 but NF90 recorded the highest retention of over 95%. The MWCO is defined as the molecular weight of a solute that was rejected at 90 percent. NF90 was rather chemical-resistant as it showed somewhat consistent performance regardless of the solution's pH. There was only a drop of about 2% of retention performance for NF90 compared to the obvious increase or reduction of retention performance shown by the rest of the nanofiltration membranes tested. The NF90 and NF270 membranes are slightly different although with the same polyamide thin-film composite. NF270 has a very thin semi-aromatic piperazine-based polyamide active layer while NF90 consists of a fully aromatic polyamide active layer (Ngiam *et al.*, 2004) while NTR7250 is made of a combination of poly vinyl alcohol and piperazine trimesamide (Nyström *et al.*, 1995).

Puasa, (Puasa *et al.*, 2006) reported that polyamide thin-film composite membranes have charge characteristics that influence the separation capabilities, which can be altered by the solution's pH and it was reported that the isoelectric point of polyamide membrane is generally between 4 and 5. According to Nyström *et al.*, (Nyström *et al.*, 1995) the isoelectric point of poly vinyl alcohol is between 3 and 4. The occurrence of an isoelectric point means that at lower pH than the isoelectric point, the membrane is positively charged and vice-versa. Hence, in the case of polymeric membranes, membrane surface charge is typically negative at high pH values, it decreases as the pH decreases and switches to positive values at low pH's (Bandini and Mazzoni, 2005).

### 3.1.2 Retention of Herbicides in Presence of Organic Matter and TiO<sub>2</sub>

In the membrane separation experiments in which humic substances and TiO<sub>2</sub> were mixed together with herbicides, the final feed solutions were first prepared and placed in a foil-covered container (to prevent herbicide degradation by exposure to light) and stirred for 24 h, after which they were assumed to be at equilibrium - a protocol used by earlier researchers (Devitt *et al.*, 1998). The nanofiltration experiments show influence of humic acids acting on the retention of atrazine as shown in Figure 5.

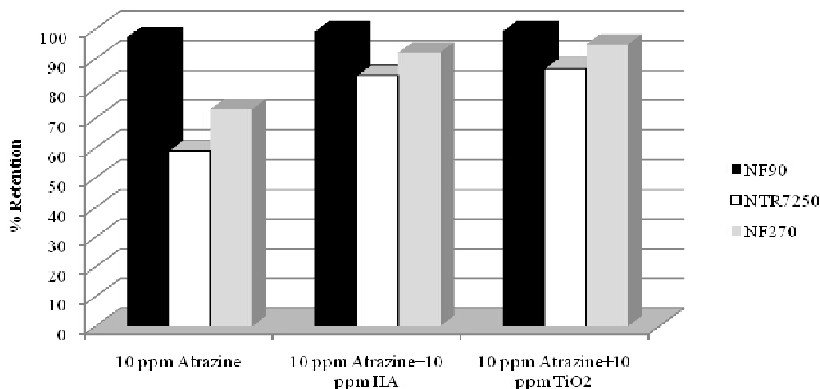


Figure 5: Membranes retention performance in presence of HA and  $TiO_2$ , s; pressure 12 bar, velocity 2.5 m/s, temperature 25°C and pH 8.3

This is attributed to the formation of complexes between humic acids and atrazine, which enhance the rejection by steric exclusion. According to Chiou *et al.*, (1986) hydrophobic humic substances of high molecular weight are not very soluble in water and display a stronger interaction with non-ionic complexes like atrazine. This interaction between herbicides and humic substances can be attributed to the large number of functional groups characterizing the structure of humic materials.

The effect of humic substances on atrazine adsorption and retention is in agreement with other studies; the explanation is that a low energy bond between humic substances and atrazine is established by physisorption which results in an increased steric exclusion of the humic substance-atrazine pseudocomplex (Kulikova *et al.*, 2002, Plakas *et al.*, 2006). Moreover, the density of the complex negative charge increases due to the primary negative charge of humic substances, while the adsorbability of the complex on the surface of the membrane is enhanced due to the hydrophobic nature of humic acid.

The nanofiltration experiments in which  $TiO_2$  was mixed with atrazine show little effect on retention of atrazine by the membranes. This was caused by adsorption of atrazine on the surface of the catalyst forming large complexes which facilitated rejection by molecular sieving effect.  $TiO_2$  catalyst has been reported in many studies for its effectiveness in degradation of organic matter. It has been noted in previous studies that photocatalytic process mainly occurs on the catalyst surface and not in the bulk solution (Li *et al.*, 2002) hence the first step is adsorption on catalyst surface. In presence of HA and catalyst all membranes recorded retention of over 80%.

### 3.2 Influence of Solution pH, Feed Pressure and and Concentration

Figure 6 shows the flux of the membranes during atrazine filtration. Based on Fig. 6, it was obvious that the increase in pressure had significant effect on the permeate flux in the atrazine filtration tests. All membranes tested experienced approximately double increment of permeate flux when the operating pressure was doubled from 6 bar to 12 bar. This shows that permeate flux increment corresponded to the pressure applied to the solution and, therefore, concentration polarisation and fouling did not affected the filtration performance. Meanwhile, concentration of feed showed slight decrease of flux i.e., we are already above critical flux.



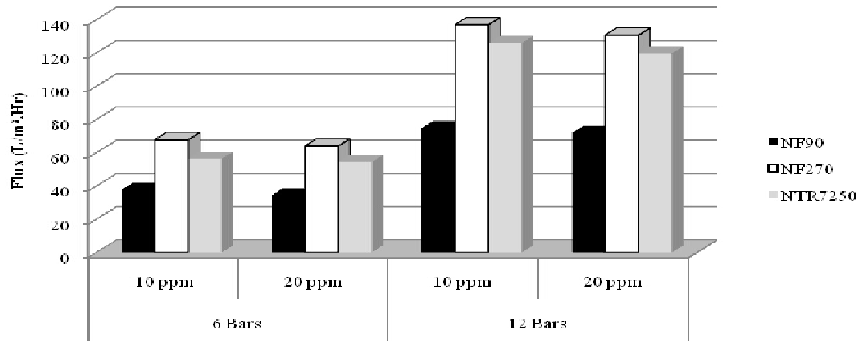


Figure 6: Membranes flux performance at temp. 25°C, velocity 2.5 m/s, pH 8.3

NF270 produced the highest permeate flux for all conditions tested while NTR7250 showed the second highest. NF90 showed the lowest permeate flux among the membranes. Based on the published data, NF270 had average pore size of 0.71 nm, NF90 had average pore size 0.55 nm while NTR7250 had average pore size of 0.65 nm (Plakas *et al.*, 2008, Zhu *et al.*, 2003). Hence, the results obtained in this study agreed with the average pore size reported in the literature, that the pore size has an influence on membrane permeate flux. However, this also showed that while 0.55 nm average pore size of NF90 was sufficient to retain atrazine with high percentage of rejection, solute-membrane interaction factor was also important (Bellona *et al.*, 2004, Kim *et al.*, 2005) as NF270 showed better retention than the NTR7250. The effect of solution pH on permeate flux is shown on Figure 7.

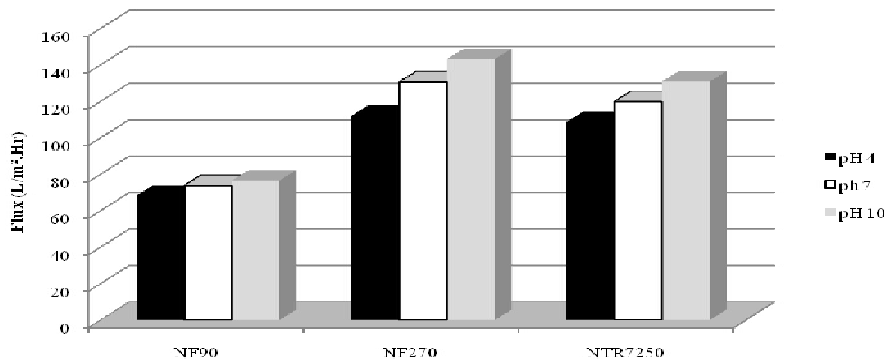


Figure 7: Membranes flux performance as a function of solution pH, at temp. 25°C, vel. 2.5 m/s, pressure 12 bars, pH 8.3 and atrazine concentration 10 ppm

In all the membranes tested, the permeate flux was somewhat lower at pH 4 and at pH 7 while pH 10 recorded the highest permeate flux. This was probably caused by changes on membrane surface charge. It has been reported in several studies that above membranes isoelectric point, the negative surface charge of membrane increases. (Armad *et al.*, 2008, Nyström *et al.*, 1995). Hence, at high pH values the membrane becomes more hydrophilic and vice versa at low pH values. Increase in membranes hydrophilicity causes more water to permeate through the membrane pores resulting higher flux (Mänttari *et al.*, 2006).

### 3.3 Influence of HA and TiO<sub>2</sub> on Permeate Flux

The presence of HA in atrazine feed solution caused a decline in permeate flux while TiO<sub>2</sub> showed insignificant decline in flux as shown on Figure 8.

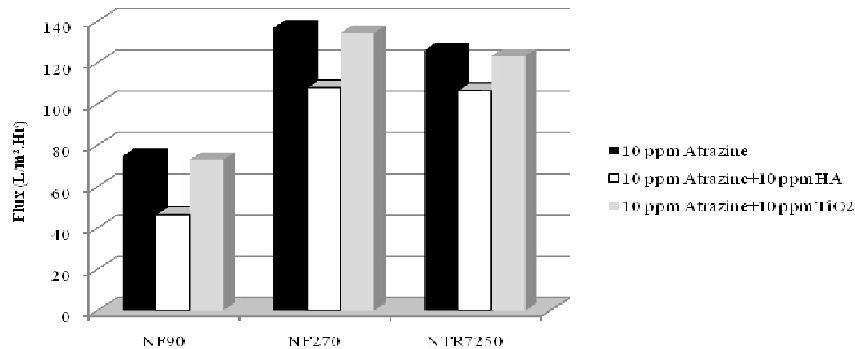


Figure 8: Membranes permeate flux performance in presence of HA and TiO<sub>2</sub>, at temp. 25<sup>o</sup>C, crossflow velocity 2.5 m/s, pressure 12 bars, pH 8.3

The permeate flux decline caused by HA was evident in all membranes tested. HA is hydrophobic and adsorbs easily on membrane surface. This adsorption leads to reduction in effective pore size causing reduction in permeability of the membrane. The organic matter adsorbs on TiO<sub>2</sub> surface and in the presence of light is degraded

#### 4.0 Conclusion and Recommendations

The performance of nanofiltration membrane to retain atrazine in aqueous solution was examined in this study. Three nanofiltration membranes, NF90 and NF270 which have molecular weight cut-off of around 200 g/mol and NTR7250 with MWCO between 300 -450 g/mol, were subjected to laboratory crossflow filtration tests and the effects of feed concentration, operating pressure, pH, presence of HA and TiO<sub>2</sub> on the permeate flux and retention of atrazine were investigated. It was found that increasing the transmembrane pressure posed positive effect on atrazine retention and permeate flux.

However, the effect of feed concentration had negligible influence on the performance of the membranes tested. The pH of feed solution had influence on permeate flux and retention of the membranes tested. The best retention was achieved at pH 7 and lower at pH 4 and 10. Polar components such as pesticides have a lower retention when the membrane charge increases, because they are dipoles which can have a preferential orientation towards the membrane in the sense that the side of the dipole with a charge opposite to the membrane charge is the closest to the membrane. In this way, the preferential orientation results in an increased attraction, an increased permeation and thus a lower rejection. On the other hand, permeate flux increased with increasing pH and was attributed to changes in the surface charge of the membrane characteristics. Above the membranes isoelectric point (high pH), it became more hydrophilic hence more water permeated through and vice versa at low pH. In presence of humic substances, the rejection was found to increase while the flux declined which was attributed to adsorption of HA on the membrane surface, thus, narrowing down the membrane pores. TiO<sub>2</sub> presence led to an increase in rejection and did not much affect the permeate flux.

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