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OPTIMIZING THE NANOFILTRATION OPERATING CONDITIONS AS POST TREATMENT STEP IN THE GROUNDWATER DENITRIFICATION PROCESS

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Abstract

Two types of nanofiltration membranes had been used to study the influence of cross flow velocity on the membrane filtration of denitrification effluent (NF270 and NF90). Filtration had been conducted at constant transmembrane pressure of 5 bar and variable cross flow velocity (0.03, 0.06, 0.15 and 0.39 ms^{-1}). The obtained normal flux was 0.47, 0.58, 0.59 and 0.77for NF270 membranes and 0.35, 0.38, 0.41 and 0.39 for NF90 membranes, the increase in cross flow velocity had enhanced flux performance of NF270 membranes more than NF90. The structure of the accumulated particles on the membrane surface had changed with each increment in the cross flow velocity, the accumulated particle count had decreased on the following percentages 35.65, 43.54 and 56.62% for NF270 and 34.85, 40.10 and 46.71% for NF90 membranes. The achieved active biomass concentrations was 4.65E+07, 1.96E+07, 1.70E+07 and 1.29E+07 $ng.m^{-3}$ on the NF270 membranes and 7.78E+07, 4.41E+07, 3.74E+07 and 3.54E+07 on NF90. The cross flow velocity higher than 0.06 ms^{-1} had minor influence on the bioparticles removal rate comparatively to non bioparticles.

Key words: denitrification, membrane, normal flux, particles size distribution, bioparticles

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1. Introduction

Biological denitrification had been considered the most effective process for nitrate removal in comparison to other treatment process, like electrodialysis, ion exchange, and reverse osmosis (Annouar et al., 2004; Bohdziewicz et al., 1999; Crespo et al., 2004; Huang et al., 1998; Mallevialle et al., 1996; Menkouchi et al., 2008; Pintar et al., 2001), biological treatment removes nitrate under anoxic conditions (Bouwer et al., 1998), denitrifying bacteria are capable of using the oxygen bound in nitrate as a terminal electron acceptor and nitrogen is released as gaseous N_2 (Barreiros et al. 1998; Ong et al., 2000). In addition, biological denitrification is the only process that directly targets nitrate and does not shift the concentration of other ions. For these reasons, biological treatment represents a cost-effective alternative. Nevertheless it suffers from certain disadvantages (Fuchs et al., 1997).

The denitrification process require further Post-treatment to remove dissolved organic carbon (DOC) and sloughed biomass from the biological reactor effluent (Ergas et al., 2004; Mara and Horan, 2003). Released bacterial cells have to be carefully removed from the treated water. This requires an intensive post treatment process, including several filtration steps and subsequent disinfections. Sand filters as well as the bioreactor have to be back washed periodically to remove the excess of biomass.

With the proven success of membranes in water treatment, there are many limiting factors like the membrane chemical stability (Hills, 2000), concentrate treatment (Squire et al., 1997; Van der Bruggen et al., 2003), running cost (Avlonitis et al., 2003; Ghabayen et al., 2004). Still the membrane

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fouling is the main limiting factor in the field of water treatment. Fouling will lead to higher operational cost, higher energy demand, increase of cleaning and reduced life time of the membrane elements (Vrouwenvelder et al., 2003). In general, fouling occurs either on the surface of a membrane or within its pores, and it causes a decrease in flux. The colloidal particles of any biological effluent cover a wide size range, from a few nanometers to a few micrometers, such as clay minerals, colloidal silica, iron, aluminium, and manganese oxides, suspended and dissolved organic matters, and calcium carbonate precipitates (Ahn et al., 1998; Nagaoka et al., 1996; Ognier et al., 2002; Stumm, 1992).

The material that fouls the membranes is diverse and is composed of inorganic, organic and bacterial cells (Al-Ahmad and Aleem, 1993; Flemming, et al., 1997). The factors that influence the membrane filtration process are (a) the hydraulic parameters which includes the cross flow velocity, transmembrane pressure and the configuration of the membrane unit(b) membrane characters such the membrane surface roughness, membrane charge, thickness and membrane permeability (c) surface loading rate which is influenced by the water quality, the filtration time, the characteristics of the accumulated mass like the particles density, shape, size, polydispersity of the particle size distribution and the osmotic pressure concentration

During membrane cross flow filtration, the colloidal particles within the feed stream are convectively driven to the membrane surface where they accumulate on the membrane surface or within the membrane pores and adversely affect both the quantity and quality of the product water and tend to form a cake or gel layer (Belfort et al., 1994; Dal-Cin et al., 1996; Zhu et al., 1995). This formed cake layer increases the hydraulic resistance to the permeate flow; as a result the permeate flux declines with time (Cheryan, 1998).

The extent of pore plugging and cake layer formation depends on the relative size of the particles compared to the membrane pore size. At the same sequence the structure of the formed cake layer involves the combined physical, chemical, and biological characteristics of the of the deposited particles, due to that it might be controlled by proper operation parameters, such as shear force induced by the cross-flow velocity (Defrance et al., 1999; Nagaoka et al., 2000; Tanaka et al., 1994). While the properties of the membrane fouling can be characterized by (a) the level of internal and surface fouling, (b) the cake height, (c) the accumulated mass, (d) the porosity and (e) particle size distribution (PSD).

When a suspension in the membrane feed stream contains particles larger than the membrane pores, then a sieving mechanism is dominant and a cake layer of rejected particles will be formed on the membrane surface. The cake layer provides an additional resistance to filtration and the permeate flux declines with time.

The cake layer and membrane may be considered as two resistances in series, and the permeate flux is then described by Darcy's law (Eqs. 1-4) (Choo et al., 1996).

$$J = \frac{1}{A_m}\frac{dV_p}{dt} \quad (1)$$

$$J = \frac{\Delta P}{\mu R_t} \quad (2)$$

$$J = \frac{\Delta P}{\mu\left(R_m + R_c\right)} \quad (3)$$

$$J = \frac{J_m}{\left(1 + R_c/R_m\right)} \quad (4)$$

where: A_m is the filtration area, V_p permeate volume, t is the filtration time, ΔP is the transmembrane pressure, μ is the viscosity, R_t is the total resistance, R_m is the membrane resistance, R_c is the cake resistance, and $J_m = \Delta P/\mu R_m$ is the water flux through the unfouled membrane.

Membrane fouling had been classified by many researcher into reversible and irreversible fouling (Ahn et al., 1998; Dal-Cin et al., 1995; Defrance 1999; Ognier et al., 2002; Tardieu et al., 1999), R_c can be subdivided into reversible and irreversible reversible fouling resistance, R_{cr} due to loosely attached foulants to the membrane surface and it can be easily removed by increasing the cross flow velocity and the irreversible fouling (R_{cir}) due to strong attachment foulants (i.e., pore blocking, strong cake, gel and biofilm) (Eq. 5).

$$R_c = R_{cr} + R_{cir} \quad (5)$$

Many studies had been conducted in the field of cross flow filtration of particulate suspensions; the reports of these studies often deal with prepared particles suspensions of well-defined and uniform characteristics which does not present the real situation of water samples, particularly the biologically treated water samples, since it involves particles with a wide range of variations particularly the ratio of biomass to the particles count. There is a need to develop further understanding of cross flow filtration of particulate suspensions at variable hydraulic conditions.

In this research, the optimum operating conditions of cross flow filtration had been tested for the colloidal effluent of denitrification reactor as a post treatment option. This aim can be achieved by measuring the impact of various cross flow filtration on the membrane performance due to the compounds that could be present in the treated water, and the influence of various cross flow velocities on the formed cake layer.

2. Materials and methods

2.1. Preparation of suspended biomass

Suspended denitrification process for ground water had been conducted with real contaminated nitrate ground water; the contaminated ground water with 60mg/L had been collected from Bisamberg - North of Vienna-Austria.

The effluent of the denitrification effluent had been gathered in separate tank, the large agglomerated flocks had been removed by passing the water through sieve opening of 0.5 mm, before it had been feed to the tank of the filtration unit.

2.2. Membrane types and filtration unit

Two different types of Nanofiltartion membranes NF90 and NF270 from Filmtec Company had been used in the experiments. The membrane filtration unit as shown in Fig. 1, consists of filtration tank with 20 liters capacity coupled with heat exchanger to stabilize the feed water at 20°C+/-, the holding tank had been connected to variable speed pump by a vacuum tube, the gear pump model is VG300 produced by VERDER company, pressure tubes had been used to connect the filtration cell to the gear pump. The dimensions of the active membrane filtration unit (length, Width, Depth) are (260, 57, 1.2 mm).

The permeate flow rate of the filtration cell had been measured gravimetrically with Sartorius analytical balances, model ED4202s-CW, the balance connected to PC, where data signal from balance has been acquired via LABVIEW every 5 second intervals and manipulated inside that program. The concentrate flow rate had been measured with Rotameter and it had been recycled to the Filtration tank.

2.3. Filtration experiments

For each membrane type there was four filtration runs; each filtration run with new membrane piece at fixed transmembrane pressure of 5 bar, but variable cross flow velocity (0.02, 0.06, 0.15 and 0.39 m/s) as listed in Table 1.

The membranes had been soaked in distilled water over night, the water had been replaced every 8 hours. After the membrane had been installed in the filtration unit, it had been flushed with distilled water for 30 minutes without recycling to the holding tank, later the membranes had been flushed for another 30 minutes with recycling. After the flushing process is completed, the holding tank had been emptied and filled with new distilled water for determining the pure water flux.

Pure water flux for each membrane type had been measured at constant transmembrane pressure but variable cross flow velocity as in Table 1. After the measurement of the pure water flux of the selected membrane piece, the filtration tank had been filed with fifteen liters of the water sample (the biological treated ground water) and the same filtration procedure had been performed for the membrane piece, the duration of each filtration run with biological treated effluent was around two hours.

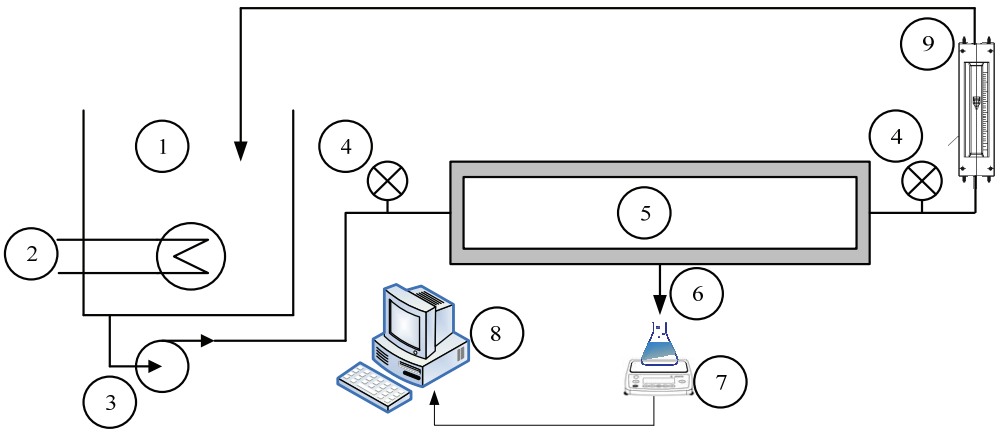

Fig. 1. Membrane unit set up (1), holding tank (2), heat exchanger (3), gear pump (4), pressure gauge (5), membrane filtration cell (6), balances (7), connecters, Pc (8), rotameter (9)

Table 1. Conducted filtration experiments for both membrane types

Run	*NF270*				*NF90*			
	bar	*Temperature °C*	*ms^{-1}*	*Re*	*bar*	*Temperature °C*	*ms^{-1}*	*Re*
1	5	20±2	0.02	750	5	20±2	0.02	750
2	5	20±2	0.06	1,874	5	20±2	0.06	1,874
3	5	20±2	0.15	4,498	5	20±2	0.15	4,498
4	5	20±2	0.39	21,620	5	20±2	0.39	21,620

2.4. Measurement and characterizing the detached mass from membrane surface

The formed cake layer on the used membranes had been characterized for each filtration run by detaching and analyzing the accumulated layer. After the filtration time is completed the detachment of the accumulated layer (biomass, organic and inorganic particles) had been conducted by replacing the used membrane in glass tube with autoclaved distilled water followed by a series of repeated low energy sonications each for the duration of 5 minutes.

The produced emulsion of the detached particles had been characterized by measuring; the particles size distribution, the particles intensity (particle count in kilo count) with dynamic light scattering method, the used instrument for dynamic light scattering was (Zeta pals 90, Brook Haven instrument cooperation).

For the same detached emulsion, the active biomass concentration was determined as adenosine triphosphate (ATP), ATP analysis is based on extraction of the compounds from biomass using a nucleotide-releasing agent followed by the light-generating luciferine–luciferase reaction. The generated light signal is measured as relative light units (RLU) after a 2s delay time and a 10 s integration time with a luminometer (Berthold).

3. Results

The filtration at different cross flow velocity for each membrane type (NF270 and NF90) had produced different fluxes for the same biological effluent as shown Fig. 2. The normal flux of each membrane piece had been calculated by dividing the flux of the biological effluent by the distilled water flux of the same membrane piece.

The average overall normal flux along the filtration time was (0.34, 0.37, 0.40 and 0.39) for NF90 membranes and (0.46, 0.58, 0.59 and 0.76) for NF270 membranes. The increase in cross flow velocity had enhanced the performance of NF270 membranes more than NF90, the achieved fluxes due to the filtration of the biologically treated ground water at different cross flow velocities was lower than initial flux value (pure water flux) in the following orders 53.04, 41.82, 40.64 and 23.04% for NF270 membrane sand 65.05, 62.01, 59.06 and 60.50 % for NF90 membranes, the increase in cross flow from 0.03 to 0.06 m/s had improved the flux value of the NF90 membrane but the further increase in cross flow velocity had not created any significant influence on the flux value in comparison to NF270 membrane as listed in Table 2.

The rejection capacity of the NF270 membranes had increased with the first increment in cross flow velocity (0.06 m/s) but the further increase in cross flow velocity had not increased the membrane rejection efficiency. For the NF90 the solid rejection efficiency was almost in the same range for all filtration runs.

The filtration of the biological effluent at different cross flow velocities had produced different recovery value for each cross flow velocity. The recovery is the ratio of the permeate volume to the applied feed volume. Table 2 summarized the average recovery value for each filtration run for both membrane types, the recovery value had decreased with the increase in cross flow velocity. The highest recovery is the recommended for economical design configuration but it is in contradiction with the flux values. Figure 3 shows the contradictory correlation between the recovery values for each flux with the correlated recovery value, for NF270 membrane.

There was an improvement in the flux performance with each increment in the cross flow velocity but the recovery value had decreased, for NF90 membrane there is a sharp decrease in the recovery value but there was no significant improvement in the flux performance after the second increment in the cross flow velocity (0.06 m/s), this cross flow velocity could be considered as the optimum cross flow velocity for NF90 membrane.

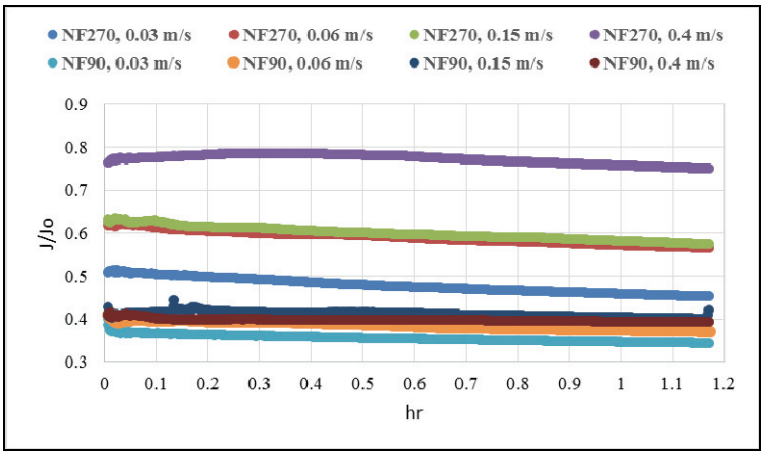

Fig. 2. Normal flux values at different cross flow velocities for NF270 and NF90 membranes

Table 2. The achieved average normal flux, recovery and solid rejection

membrane Type	*m/s*	*Normal flux*		*Revovery*		*Cake resistance*		*Solid rejection*	
		J/Jo	*STD*	*%*	*STD*	*1/m*	*STD*	*%*	*STD*
NF270	0.03	0.47	0.02	8.58	0.41	3.62E+14	1.85E+13	63.79	4.26
	0.06	0.58	0.02	4.86	0.17	2.79E+14	7.59E+12	70.53	4.61
	0.15	0.59	0.01	2.18	0.07	2.41E+14	5.33E+12	70.50	4.27
	0.40	0.77	0.01	0.98	0.02	2.29E+14	5.88E+12	73.78	4.65
NF90	0.03	0.35	0.01	4.71	0.18	1.78E+14	1.43E+13	96.30	2.18
	0.06	0.38	0.01	2.37	0.03	9.95E+13	6.84E+12	95.91	2.30
	0.15	0.41	0.01	1.02	0.02	8.61E+13	6.39E+12	95.74	1.82
	0.40	0.39	0.00	0.43	0.01	4.11E+13	2.87E+12	94.44	1.51

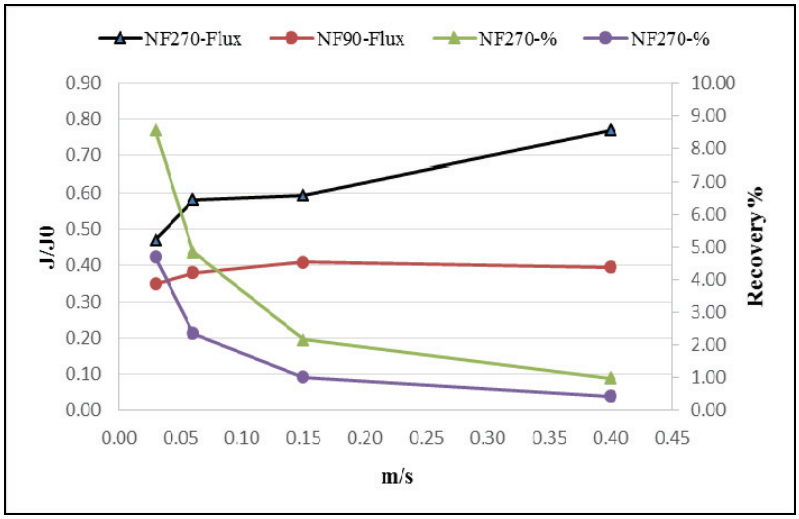

Fig. 3. Average normal flux values, recovery values at different cross flow velocities

Particles within the feed stream are convectively driven to the membrane surface by the permeate flux during the cross flow filtration. Some of these particles will be accumulated due to the convection flow, other particles will be flushed away from the membrane surface due to the cross flow velocity and this formed cake layer by particles build-up increases the hydraulic resistance to permeate flow, this resistance called the cake resistance. The average overall cake resistances of NF270 and NF90 membranes at different filtration runes are listed in Table 2. The highest cake resistance was at the lower cross flow velocity (0.03 m/s) for both membrane types, the cake resistance had decreased in different orders with each increment in the cross flow velocity.

The filtration at different cross flow velocity of the same water type will accumulate different particles with different characteristics and different particle size distribution (PSD). Figs. 4-5 shows the PSD of the accumulated particles on the NF270 and NF90 membranes at different cross flow velocities. the intensity of the smaller particles at the lower cross flow velocity (0.03 m/s) was more than at the higher cross flow velocity (0.06, 0.15 and 0.39 m/s).

The accumulated particles count on the surfaces of the used membranes in correlation to the water flux at different cross flow velocities are shown in Fig. 6. The particle count per filtered volume are expressed in terms of kilo count per filtered volume ($Kc.m^{-3}$), the highest particle count was at the lower cross flow velocity (0.03 $m{\cdot}s^{-1}$) for both membrane types, the increase in cross flow velocity from 0.03 to 0.06, 0.15 and 0.39 $m.s^{-1}$had decreased the accumulated particle count for both membrane types, the reduction on the accumulated particle count in the surfaces of the used NF270 membranes was 35.65, 43.54 and 56.62 %, for NF90 membranes the reduction in the accumulated particle was 34.85, 40.15 and 46.71%. The influence of cross flow velocity in reducing the accumulated particle count was higher in the NF270 membrane than NF90 membranes, same results had been obtained for the measurement of the accumulated active biomass as shown in Fig. 7. The biomass accumulation had been expressed in terms ATP per filtered volume (ATP/m^3).

The increase in cross flow velocity had decreased the accumulated biomass per filtered volume for both membrane types, the reduction was 57.84, 63.49 and 72.19%for NF270 membranes. For the same operating conditions, the reduction in the accumulated biomass was 43.28, 51.91 and 54.46 % on the surfaces of the used NF90 membranes.

4. Conclusion

The increase in cross flow velocity had improved the flux performance of NF270 membranes. The increase in cross flow velocity

above 0.06 m/s had a minor influence in NF90 flux value, the flux was almost in the same range due to the nature of the accumulated particles.

The accumulated particle count had decreased with each increment in cross flow velocity for both membrane types.

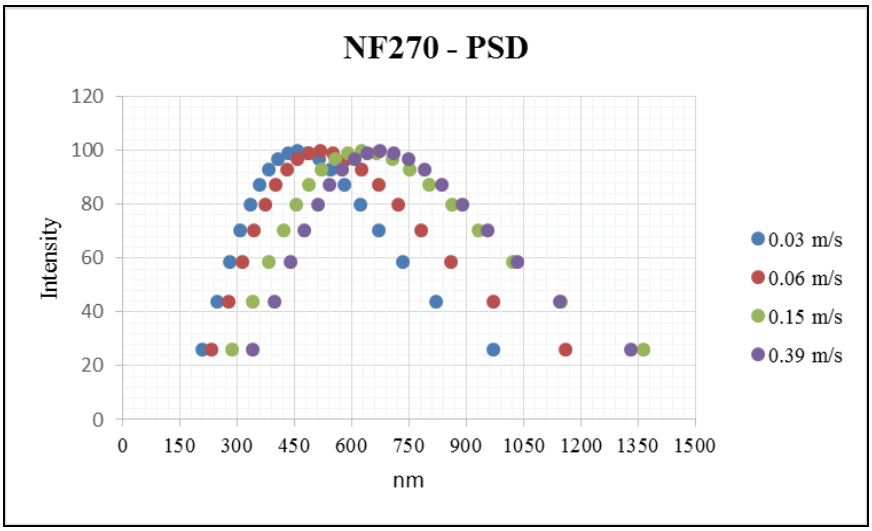

Fig. 4. NF270, particle size distribution (PSD) at different cross flow velocities

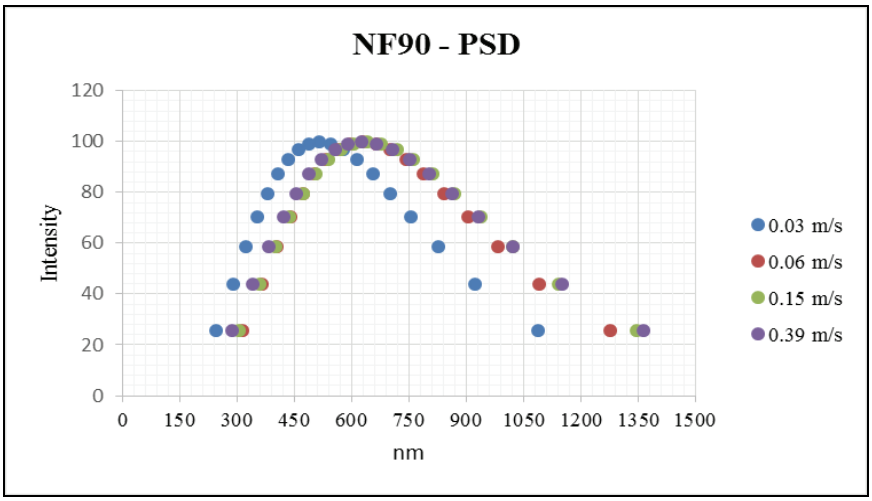

Fig. 5. NF90, particle size distribution (PSD) at different cross flow velocities

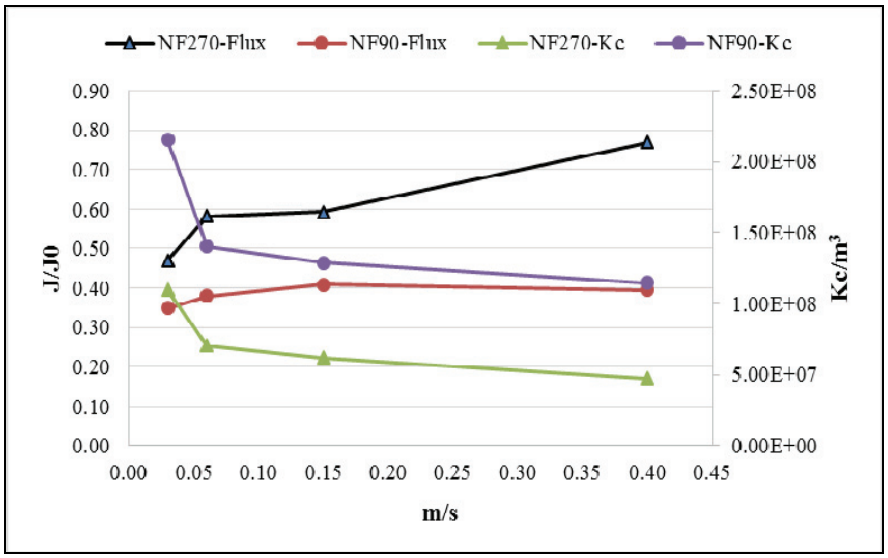

Fig. 6. Correlation between the accumulated particle count and membrane flux

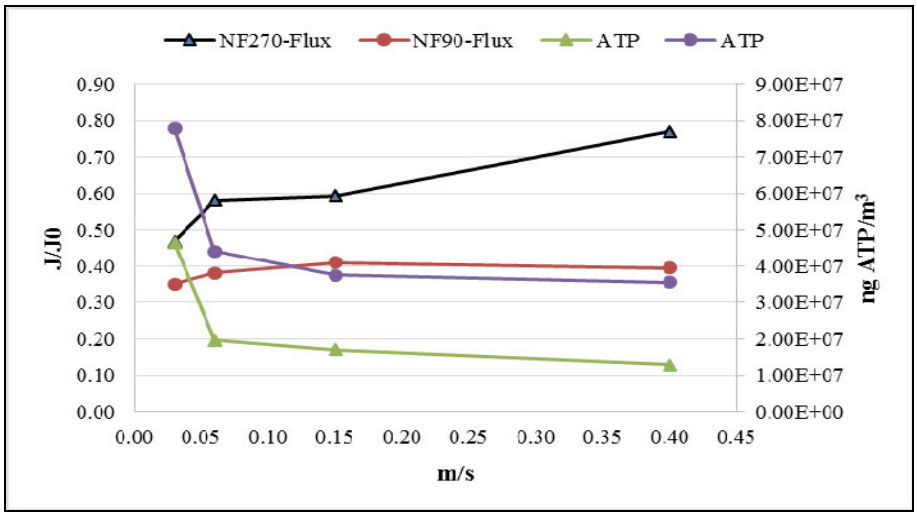

Fig. 7. Correlation between the accumulated active biomass and membrane flux

In the same sequence the accumulated active biomass concentration had decreased with each increment in cross flow velocity for NF270 membranes, the filtration at cross flow velocity higher than 0.06 ms^{-1} had no reasonable influence on the biomass concentration based on that it is considered the optimum cross flow velocity for the NF90 membranes.

For the NF270 membrane, the cross flow velocity 0.06 ms^{-1}can enhance the flux performance and eliminate the membrane fouling, the selection of the optimum cross flow velocity will be mainly dependent on the desired recovery of the filtration process.

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