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EXPLOITING THE REMEDIATION CAPACITIES OF MICROBIOLOGICAL STRAINS AND MEMBRANE TECHNOLOGIES FOR THE TREATMENT OF TEXTILE DYES EFFLUENT

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ABSTRACT
The present work evaluates the potentials of using indigenous microbial strains isolated from wastewaters of an effluent treatment plant of a Textile Industry and the feasibility of employing nanofiltration (NF) membrane and reverse osmosis (RO) systems as an alternative treatment method of textile wastewater discharged from textile industry. Experiments were performed in a laboratory - scale set up using four potential candidates' microbial strains, in which the bacterial strains (Pseudomonas monteilii and Aeromonas hydrophila) and the fungal strains (Phanerochaete chrysosporium and Aspergillus oryzae) were selected based on their ability to decolorize and degrade dyes effluent into non-toxic form. Decolorization efficiencies of the microbial strains were measured as a function of the operational parameters (aeration, dye concentration, pH, temperature, total viable count and optical density) and the microbial isolates showed increase in cell number as the concentration, absorbance and pH decreases. The effects of dye concentration, pH of solution, feed temperature, dissolved salts and operating pressure on permeate flux and dye rejection were studied using the membrane technologies. Results at operating conditions of dye concentration of 60 mg/L, feed temperature of 38 °C and pressure at 8.5 bar showed the final dye removal with NF membrane as 97.3 %, 99.1 % and 98.9 % for organic dyes, Congo red and Direct blue 80, respectively. While with RO membrane, the final dye removals were 97.5 %, 97.7 %, and 98.6 % for organic dyes, Congo red and Direct blue 80 dyes, respectively. Higher color removal was achieved due to the existence of NaCl salt in the solution. It was later confirmed that pH of solution also had a positive impact on dye removal. A comparison was made between the results of dye decolorization in microbial and membrane methods and it was found that the use of membrane technologies in dye removal from the effluent of textiles industry was highly effective and promising.

Key words: *Decolorization, microbial strains, nanofiltration, reverse osmosis, textile effluent*

1. Introduction

The textile organic dyes must be separated and eliminated where necessary from water, especially from industrial wastewaters by effective and viable treatments at sewage treatment works or on site following two different treatment concepts as: (1) separation of organic pollutants from water environment, or (2) the partial or complete mineralization or decomposition of organic pollutants. Separation processes are based on fluid mechanics (sedimentation, centrifugation, filtration and flotation) or on synthetic membranes (micro-, ultra- and nanofiltration, reverse osmosis) (Oller *et al.,* 2011; Carmen and Daniela, 2012; Molinari *et al.,* 2016). Additionally, physico-chemical processes (i.e. adsorption, chemical precipitation, coagulation-flocculation, and ionic exchange) can be used to separate dissolved, emulsified and solid-separating compounds from water environment (Robinson *et al.,* 2001 ; Carmen and Daniela, 2012; Suteu *et al.,* 2012).The partial and complete mineralization or decomposition of pollutants can be achieved by biological and chemical processes (biological processes in connection with the activated sludge processes and membrane bioreactors, advanced oxidation with ozone, H_2O_2, UV) (Dos Santos *et al.,* 2004; Hubbe *et al.,* 2016). A textile operator will decide on options available to plan onward strategy that will ensure compliance with the environmental regulators' requirements on a progressive basis focused on some options and applied solutions of different separation processes (sedimentation, filtration, membrane separation), and some physico-chemical treatment steps (i.e. adsorption; coagulation-flocculation with inorganic coagulants and organic polymers; chemical oxidation; ozonation; electrochemical process, etc.) integrated into a specific order in the technological process of wastewater treatment for decolourization or large-scale colour and dye removal processes of textile effluents (Holka *et al.,* 2016; Yao *et al.,* 2016).

The present work will focus on microbial decolorization and separation by two types of pressure-driven membranes which are nanofiltration (NF) and reverse osmosis (RO) membranes. NF is characterized by a membrane pore size between 0.5 and 2 nm and operational pressures between 5 and 40 bars. It is used to accomplish separation between sugars, other organic molecules and multivalent salts on one hand and monovalent salts, ions and water on the other (Abid *et al.,* 2012; Afzali *et al.,* 2016; Yu *et al.,* 2016). RO or hyperfiltration is characterized by a membrane pore size in the range of 0.5 nm. The working pressures in RO are generally between 7 and 100 bars (Abid *et al.,* 2012;

Afzali *et al.,* 2016, Yu *et al.,* 2016). The significance of these membrane processes can be resolved from the membrane area fitted in various industrial sectors. The ability of RO membranes to remove both organic and inorganic compounds has made it striking for the treatment of contaminated drinking water supplies (AWWA, 1992; Brandhuber and Amy, 1998). Reverse osmosis processes can instantaneously remove hardness, color, many kinds of bacteria and viruses, and organic contaminants such as chemicals used in agricultural processes and trihalomethane precursors.) The combination of NF/RO for nitrate removal would suffer less from scaling than a single RO because of $CaSO_4$ and $CaCO_3$ removal in the NF step (Bohdziewicz *et al.*, 1999; Ribera Simon, 2013). Cristiane *et al.* (2005) studied the application of nanoafiltration process mainly in the rejection of color and chemical oxygen demand (COD) present in textile industry wastewater. The results of the tests showed the values for color rejection were around 99 % and 87 % for COD rejection. The process was efficient and promising for the reuse of wastewater for this type of industry. Al-Aseeri *et al.* (2007) investigated the removal of sodium chloride and acid red dye from aqueous solutions. Acid dye concentrations, n = 3 (0.10, 100 and 200 mg/L) and NaCl concentrations, n = 3 (100, 1000 and 5000 mg/L) were used. Results showed that in the absence of NaCl, color removal of 97.2 % was achieved and this number was elevated to 98.2 % at dye concentration of 200 mg/L, when 1000 mg/L NaCl was added to the colored water. Avlonitis *et al.* (2008) investigated the effluents from the cotton textile industry which were treated by nanaofiltration membrane in order to reduce the quantity of the disposed water and at the same time to reuse the treated water. Results showed that NF membranes could achieve complete decolorization of the cotton dye effluent and reduced the total salt concentration more than 72 %. These membranes can be used even at high recoveries and reasonably low pressures, producing high quality water, which can be reused.

Currently, microbial method has been utilized in the treatment of wastewater containing synthetic dyes used by textile industries worldwide. The present work is devoted to study both the microbial decolorization and the operating feasibility of pressure-driven membrane system as an alternative treatment method of such wastewaters.

2. Materials and Methods

2.1 Samples collection and chemicals

The two reactive dyes of relatively simple structures were chosen for this work and are commonly used dyes in textile industries. The characteristics of these dyes are presented in Table 2. , Congo red (% purity 60) and trimethylmethane usually called Malachite green (% purity 70). The percentage purity was obtained from Aldrich Chemical Company (Milwaukees, Wis), as was Congo red in a 90 % pure form. Analytical grade chemicals HCl 36 %, H_2SO_4 98 % and NaOH employed in the experiments were at least reagent grade were used to adjust feed pH and to clean the membranes. While the textile effluent samples were collected directly from the confluent unit of the textile wastewater discharge canal of the textile industry in sterile containers. The samples were transfer to the laboratory and processed 48 hrs. These samples were used in isolation of microbes and treatment trials.

2.2 Pretreatment of the Sample

A filter paper was folded and inserted on the mouth of the soxhlet extractor unto which some quantity of XAD-2 resin was carefully dispensed. 2.5 liters of textile wastewater was measured using graduated cylinder and carefully dispensed in the XAD - 2 resin. The organic components of textile waste effluent were retained within the organic resin as residues and the filtered were collected and discarded. The resulting residues as the desired component need for the analyses were allowed to dry for 2 hrs within the soxhlet extractor.

A measured volume of 50 cm^3 ether was passed through the dried residues of XAD - 2 resin contained in the soxhlet extractor, and all the organic components in the XAD - 2 were miscible with ether as organic solvent which are collected as a filtered and were warm gently in a hot air oven at 180 ^oC to allow the ether to evaporate in 48 min. The solid deposit was allowed to cool to 35 ^oC and weighed to 30 g which were diluted to 1000 cm^3 with sterile de-ionized water and properly labeled as a stock solution (1000 mg/dm^3).

2. 3 Experimental Apparatus

The experiments were performed on a pilot plant scale. A test skid unit was arranged according to Abid *et al.,* 2012 as shown in Figure 1.

Two types of membranes, (NF) and (RO) were used. Each membrane was mounted in turn into stainless steel casing. The characteristics of NF and RO membranes are shown in Table 1. The liquid was dispersed through the pilot plant by two pumps, the low pressure pump (Type: centrifugal, Q = (30 - 100 L/min), H = 20 - 30 m) which transported the liquid solution from the feed tank to the suction of the high pressure pump by the help of micro filters of 5 μm and 1 μm, respectively. The function of the micro filters was to liberate the suspended solids and decreasing turbidity and silt density index (SDI) in the influent line to the membrane compartment (Abid *et al.,* 2012).

The pressure across the membrane housing was supplied by the high pressure pump. The pilot plant contained three holding tanks, all were made of polyethylene. These were the feed tank (500 L), the concentrate tank (500 L) and the permeate tank (125 L). Each tank was supplied with suitable fitting and connections to serve the process. Flow rate, pressure and temperature of the flowing streams were measured in the following manner. Two calibrated rotameters were used to measure the flow rate of permeate and concentrate. The pressure was measured by liquid filled bourden type gauges. Temperatures at upstream and downstream of the membrane housing were measured by dial gauge type temperature pointers with sensors type (Pt/100). The pilot plant was also supplied with two on-line instruments attached to the unit to measure electrical conductivity (EC) and total dissolved solids (TDS) of permeate and concentrate, respectively (Abid *et al.,* 2012).

In addition to the skid mounted conductivity and TDS meters, laboratory portable conductivity TDS and pH meters were used for extra check and speedy measurements.

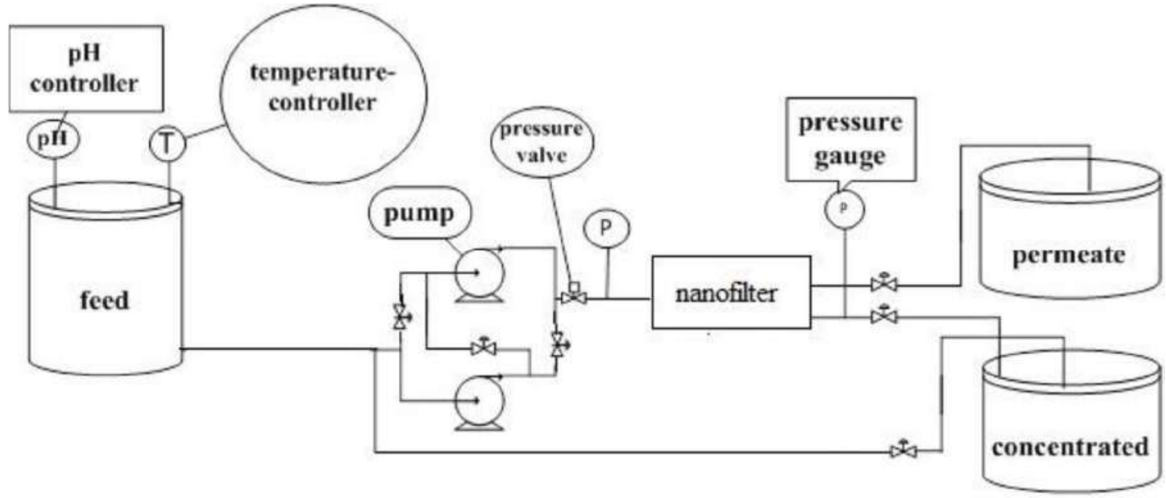

Figure 1. Schematic representation of the NF/RO experimental apparatus

2.3.1 Experimental procedure

Experiments were carried out in different steps following the method of Abid *et al.* (2012): In the first step, each dye solution was prepared in four concentrations of 60, 80, 100 and 120 mg/L in order to study the effect of dye concentration on rejection coefficient of the membrane. In the second step, the experiments were carried out at different pressures (6, 8, 10, 12 and 14 bars) for each individual concentration of every dye. In the third step, four different feeds pH (4.5, 6.5, 7 and 8.5) were investigated. The feed pH was adjusted by addition of HCl and NaOH to the feed tank. In the fourth step, two different temperatures were tested (38 °C and 27 °C) to investigate the seasonal effect on the membrane performance. Steps 1, 2, 3 and 4 were repeated using tap water as solvent to study the effect of TDS on dye removal. Sample analysis of wastewater effluent from textile industry is shown in Table 2. Table 3 shows the physicochemical analysis for tap water used in the membrane testing system. In all steps, samples were collected for analysis every 15 min. All experiments were carried out in 2 h to reach the steady state conditions.

2.4 Isolation and enumeration of microbial cultures

Total bacteria were enumerated by spread plate method using 0.1ml of the dilution 10^{-1} to 10^{-4} onto nutrient agar. All cultures were incubated for 24 hr to 48 hr at 37 ^oC. The bacterial colonies, which developed on the plate were randomly picked and purified by sub-culturing unto fresh agar plates using the streak-plate technique. Isolated colonies, which appeared on the plates, were then transferred unto nutrient agar slants properly labeled and stored as a stock-culture. The bacterial isolates were identified based on their morphology, gram reaction and their biochemical reactions.

The fungi were isolated from the water samples using Czapek dox agar unto which sterile streptomycin (50 mg ml^{-1}) had been added to suppress bacterial growth. Pure cultures of the fungi isolates were made and transferred using Czapek dox agar slants as stock cultures. The microscopic and macroscopic features of the hyphal mass, morphology of cells and spores, and the nature of the fruiting bodies were used for identification.

2.5 Mineral Salt Broth for microbial strains

Mineral salt medium 99.9 cm^3 was dispensed into 250 ml Erlenmeyer flask and distinct isolates from nutrient agar slants were picked gently using a sterile wire loop and inoculated into the mineral salt medium. The mixture was shaken and incubated at room temperature of 30 ^oC for 24 hrs. The mineral broth for bacterial isolates were kept near a freezing point in order to have a control of microbial load (inoculums size).

2.6 Growth of microbial strains in Organic Effluent

Mineral salt broth of bacterial isolates were dispensed in 99 cm^3 quantities into four 250 ml Erlenmeyer flasks which were arranged based on different dye concentration. To each flask was added 1 cm^3 of the effluent sample. The flask was inoculated at optimum temperature of a particular bacterial isolate in an incubator spun at 20 rpm for 48 hrs. Controls were run under the same reaction conditions of 99 cm^3 mineral salt broths with 1 cm^3 of effluent but excluding bacteria. The optical density (absorbance) at different wavelengths, were determined (Cheesbrough *et al.,* 2005).

2.7 Decolourization determination assay

Aliquots of 2 cm^3 of a clear dye solution were taken from each of the reaction flasks at time intervals and measured immediately using a UV-Visible recording double beam spectrophotometer. Care was taken not to draw out portions of the microbes in the aliquot. All samples from the culture medium had to be diluted prior to measurement in order to keep the change in absorbance values measured below 1.0 absorbance units per centimeter of path length. Because of the low water solubility of the organic dyes, an equal volume of methanol was mixed with the analytical solution to ensure complete solubilization prior to measurement. Decolourization was assessed in two ways; one way was by monitoring spectrophotometrically the absorbance at the wavelength maximum for each cultured solution and by the reduction of the major peak area in the visible region for each cultured solution. To obtain additional information regarding the changes, the area under the curve in the visible regions (400 - 800 nm) was integrated.

2. 8 Analytical methods for membranes

Analysis of samples was carried out based on standard methods. The colour which is a function of dye concentration was determined spectrophotometrically at a dominate wavelength by spectrophotometry method No. 2120 of Standard Methods, using a Shimadzu UV-visible spectrophotometer (UB-1201 PC) which measures the light absorbency of a dye solution. The solution conductivity was measured by portable conductivity meter (Horiba DF-H). Samples were measured by portable pH meter (HACH digital pH meter). Retention factor (R) of each species was calculated using the simple relationship (Norman *et al.,* 2008).

$$\% R = [1 - Cp/Cr] \times 100 \quad (i)$$

where R is rejection factor (%), Cp is the solute concentration in the permeate (mg/L), Cr is the solute concentration in the feed solution (mg/L), and permeates flux (Jw) of the membrane is calculated as:

$$Jw = Qp/A \qquad (ii)$$

where the 'Jw' is the permeate flux ($L/m^2.h$), 'Qp' is the permeate flow rate per hour and 'A' is active surface area of membrane (m^2).

3. Results and Discussion

The experimental design was based upon the organic components of textile waste effluent and the other two most commonly used dyes in the African Textile Company Kano were selected. The effects of dye concentration, pH of the dye solution, feed temperature, dissolved salts, and operating pressure on dye removal and permeate flux were examined. Figure 2(A & B) presents a comparison for organic components of textile dye effluent removal between the membrane separation and microbiological method. Result and other corresponding figures are presented in a way to view on the same plot, the performance of NF and RO membranes utilized herein this work. For the microbiological strains were substantially decolorized organic dye effluent, Congo red and direct blue '80' dye to 66.4 %, 68.2 % and 67.8 % respectively, in which the visible portion of the spectrum dyes showed a major peak; after 48 hrs period of treatment, this peak shifted down with an increased in total viable count. This show that when the concentration of dyes were 60 mg/L there is remarkable dye removal but when the concentration increases it shows decreased in in dye removal as shown in Fig. 2B.

On effect of concentration on dye removal, the Figure 2A-B illustrates the variation of dye removal (DR %) with dye concentration in feed for different types of dyes. As can be seen, the dye removal is positively related to the dye concentration. Result at operating condition of pH = 8.5, feed temperature = 27 ^{o}C and pressure = 8 bar showed that when dye concentration was increased from 60 mg/L to 120 mg/L, the dye removal with NF membrane was increased from 79.2 % to 97.3 % for organic components of textile dyes effluent respectively, and while RO membrane, the organic components of dyes effluent removal was increased from 73.4 % to 97.5 % respectively. As expected, for higher feed concentration, higher dye removal was achieved. This is mainly due to concentration polarization layer which is built on the membrane surface as a result of increasing dye concentration in feed and leading to higher osmotic pressure (Akbari *et al.,* 2002; Al-Bastaki *et al.,* 2007). The system with RO membrane, in which the rejection can be affected more by size exclusion than the other mechanisms, performs higher rejections than that for the system with NF membrane, as the effective hydrodynamic radius of dye molecule is typically larger than the membrane pore radius, the rejection of dye is therefore mainly controlled by sieving mechanism. Thus, it is less possible for dye molecules from passage through the membranes which have relatively smaller pore size, and NF has higher MWCO which means larger pore sizes than RO (Ismail and Lau, 2008).

The higher dye removals were obtained for reactive black and blue dyes; this may be attributed to the low solubility characteristics of these dyes compared to that of acid dye. This lower solubility resulted in membrane fouling in the end of operation. Membrane fouling may be caused by the dye adsorption on the membrane surface observed at the experimental runs, which was indicated by the presence of color on the membrane after filtration (Koyuncu, 2002).

Variation of dye removal against operating pressure is shown in Figure 3. As can be seen, dye removal followed a positive trend with the range of operating pressure studied in the present work. When operating pressure was increased from 6 bars to 14 bars, dye removal with NF membrane was increased from 86.2 % to 97.1 % for organic components of dyes effluent, respectively, and with RO membrane, dye removal was increased from 91.3 % to 98.2 % for organic components of dyes effluent, respectively. This may be attributed to mechanical compaction of membrane at higher operating pressure. Compaction is the decrease in membrane volume due to mechanical deformation upon the application of a high mechanical pressure. A change in density of the active layer of the membrane implies a change in free volume available. This will have a significant influence on transport of permeating components (Bohonak and Zydney, 2005). Mechanical compaction will normally yield an increase in the density of membrane material and decrease in pore size which will decrease the rate of diffusion of dissolved solute leading to an increase of dye removal. Many researchers of the field have studied this reversible phenomenon and their findings were in agreements with our results (Pereira, 2007; Kucera, 2010).

Sodium Chloride (NaCl) is one of the most common inorganic salts that have been widely used in dyeing process for the purpose of enhancing the degree of dye fixation onto fabric. The dissolved salt in waste stream must be treated properly before being discharged into environment (Ismail and Lau, 2008). Fig. 4 illustrates the performance of NF and RO membranes for dye removal against organic components of dye effluent concentration, using distilled water and tap water, respectively. All the experiments were carried out for 2 h, to reach the steady state conditions. As expected, increasing the salt concentration resulted in higher dye removal. This may be due to the osmotic pressure of solution which increases with salt concentration and consequently a concentration polarization layer will be built up by the salt that acts as an additional barrier to the passage of the color, it seems that the effect of concentration polarization was more for membrane with smaller pore size (i.e., RO membrane) in which case of fouling can be significant (Visvanathan *et al.,* 1998).

Another concerns is the electrostatic behavior of NF membrane which has a surface of slightly negative charge due to the sulfonic acid groups R-COO- (which is responsible for rejection of Cl- ions in dilute electrolyte solution). This electrostatic repulsion made the negative ions accumulate near the membrane surface accelerating the formation rate of the concentration polarization layer. Thus the separation performance of NF membrane system was found to be significantly dependent on the steric and charge effects. This right combination of membrane pore size (steric effect) and its effective charge density (Donnan effect) may lead to an optimum separation performance (Ali and Mohammad, 2004).

It has been known that alkaline environment always has the best condition for enhancing the degree of dye fixation during dying process, though acidic condition would also be considered for certain textile operation (Ismail and Lau, 2008). Fig. 5 demonstrates the variation of organic components of dyes effluent removal against pH of solution with NF and RO membranes, respectively. The plot illustrates a positive trend between the two variables for both membranes. It is a well-known fact that, when pH of a solution decreases, the solubility of salts present increases as well. When pH of solution was increased from 4.5 to 8.5 pH, the dye removal with NF membrane was increased from 91.2 % to 98.7 % for organic components of dyes effluent, respectively, and with RO membrane, dye removal was increased from 82.5 % to 90.9% for organic components of dyes effluent, respectively. From membrane point of view, decreasing pH of solution by addition of HCl acid would increase the solubility of salts and consequently decreases the rate of salt scaling on the membrane surface which leads to decrease the osmotic pressure of solution and consequently the dye removal decreases. On the contrary, increasing pH by addition of NaOH would accelerate the deposition rate of salt on the surface of the membrane. As mentioned earlier, surface of NF membrane has a slight negative charge, this will result an electrostatic repulsion force with OH^- ions for high pH solution. In higher pH, the electrostatic repellent force becomes strong and rejection will increase (Akbari *et al.,* 2010).

Feed temperature is another factor which affects the performance of (NF/RO) membranes. Fig. 6 shows the maximum dye removal due to increasing feed temperature with different types of dye. It shows that the increase in feed solution temperature results in lower dye removal. When feed temperature increased from 27 °C to 38 °C, the dye removal with NF membrane was decreased from 95.2 % to 91.1 % for organic components of dyes effluent, respectively, and with RO membrane the dye removal was decreased from 93.2 % to 90.1 % for organic components of dyes effluent, respectively. This may be attributed to the increase in the diffusion rate of the molecules across the external boundary layer and in the internal pores, owing to the decrease in viscosity of the dye solution in addition to increased membrane pore size (Cadotte, 1980). This increase in pore sizes is partially characterized by higher dye passage. From Fig. 7 it can be seen that the flux of acid dye is higher than that of reactive dye. This is due to the fact that molecules with smaller molar mass diffuse more easily than that of larger molar mass at the same operating conditions (Bellona *et al.,* 2007). In addition to the fact that water permeability of the membrane increases with increasing temperature. These results are in agreement with the findings of Nilsson *et al.* (2008).

Figure 7 shows a comparison of the permeate flux between NF and RO membranes for variable feed pressure at different types of dye. It can be seen that higher flux values were obtained at 14 bars for any applied dye, since the increase in feed pressure will increase the driving force, overcoming membrane resistance (Salahi *et al.,* 2010). On the other hand, the higher is the feed concentration, the lower is the permeate flux; this may be attributed to increasing the concentration polarization on the membrane surface and consequently increasing the osmotic pressure. When operating pressure was increased from 6 bars to 14 bars, permeate flux with NF membrane was increased from 0.19 to 0.5 (L/m^2.h.) for organic components of dyes effluent, respectively, and with RO the flux was increased from 0.18 to 0.47 (L/m^2.h.) for organic components of dyes effluent, respectively. Also it can be seen that the flux for the system with NF membrane is more than double that for the system with RO membrane.

This is because NF membrane has larger pore size than that of the RO membrane. The results shown in Figure 7 indicate that permeate flux of the acid dyes obtained were higher than that of the reactive dye at the same operating conditions. This is due to the decrease in solubility with the increase in molecular weight of dye applied. It should be noted that the mass increase may also be related to diffusion, because a bigger molecule will diffuse more slowly than a smaller molecule. The result of the present work seems to be in a good agreement with those observed by (Gholami *et al.,* 2003) for the effect of pressure at different dye concentrations.

The equation is the proposed empirical correlation:

$$F = a_o P^{a1} C^{a2} (pH)^{a3} (TDS)^{a4} \qquad \text{(iii)}$$

where a_1, a_2, a_3 and a_4 are constants, representing the magnitudes of the effect of applied pressure, dye concentration, pH solution, and TDS, respectively, on the objective function (i.e., dye rejection), while a0 is a constant that depends on the nature of the operating system and the objective function. The constants of this correlation with the variance and correlation coefficient are shown in Tables 5 and 6 for acid red dye removed by NF and RO membranes, respectively.

The empirical correlations

The objective response value at each average seasonal temperature is the result of the interaction of several parameters, namely: operating pressure; dye concentration; pH; and TDS. A power law formula was used to correlate the present experimental results of dye removal of organic components of dye effluent.

Tables 4 and 5 depict the order of effect of the operating variables on dye removal of NF and RO membranes in the following sequence: C > pH > P > TDS.

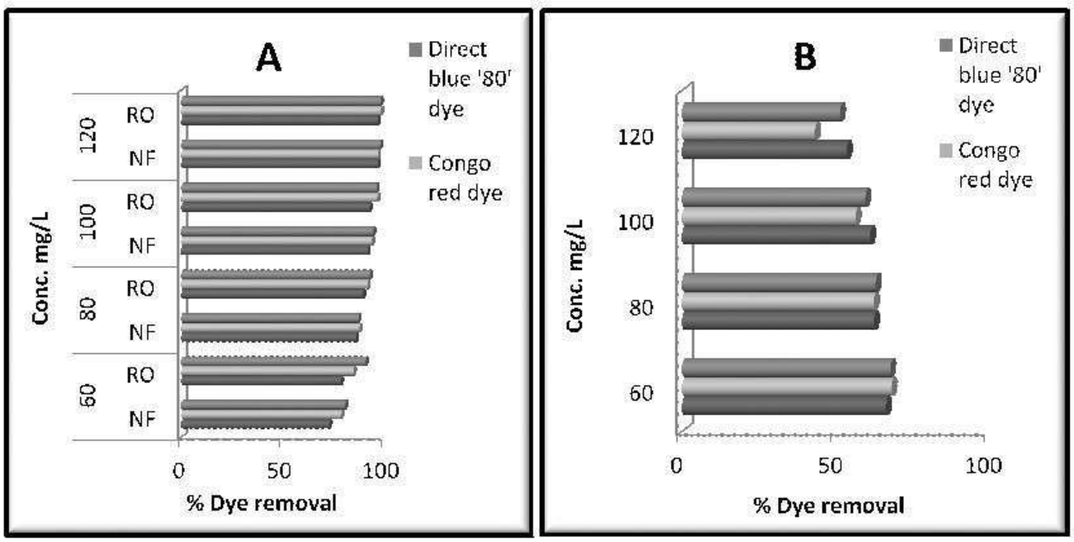

Figure 2. (A & B) Effect of dye concentration on dye removal of NF /RO membrane (2A) and Microbiological method (2B) at p = 8 bars, pH = 8.5, T = 38°C)

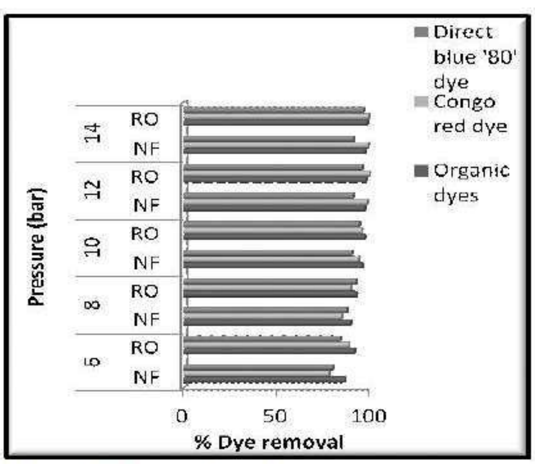

Figure 3. Effect of membrane pressure on dye removal of NF and RO Membrane (pH = 8.5 T = 27°C)

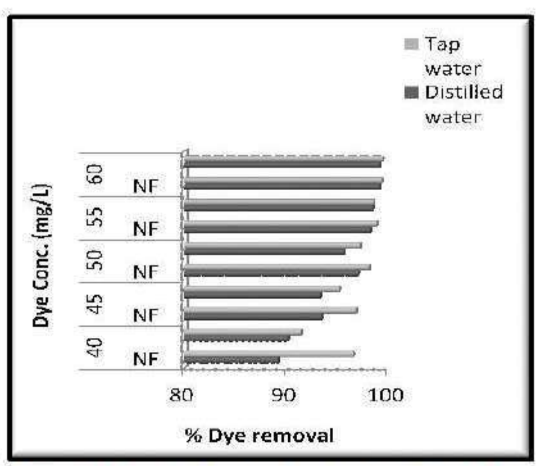

Figure 4. Effect of dye concentration on organic dye effluent removal of NF and RO membrane with tap and distilled water (p= 10 bars, pH= 8.5, T = 27°C)

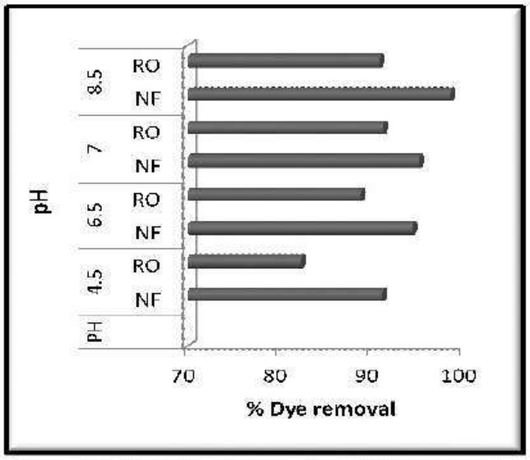

Figure 5. Effect of pH on acid red dye removal of with NF and RO membranes (C = 50 mg/L, p = 8 bars and T = 27° C)

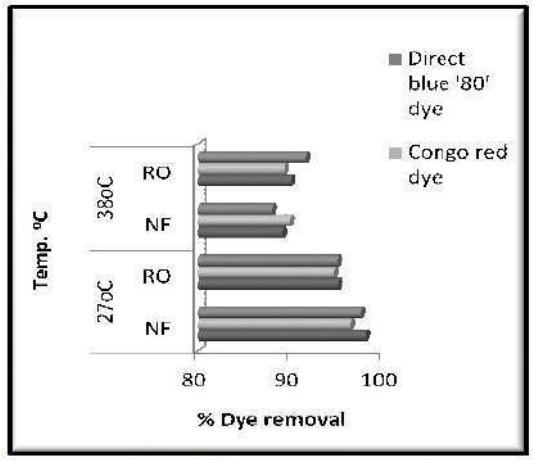

Figure 6. Effect of feed temperature on dye removal with NF and RO membranes at different types of dye (p = 8 bar and T = 27° C)

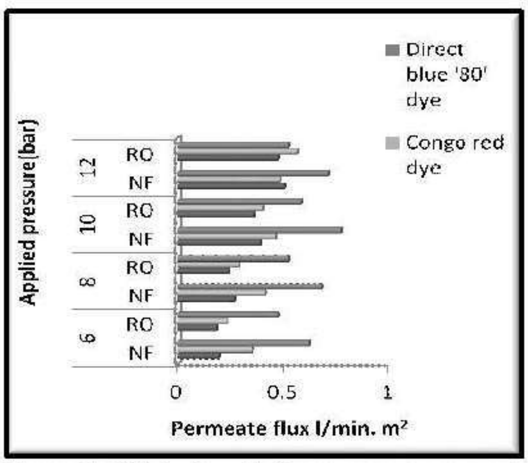

Figure 7. Effect of applied pressure on permeate flux of RO and NF membranes using different types of dye (C = 50 mg/L, pH = 8.5 and T = 27°C)

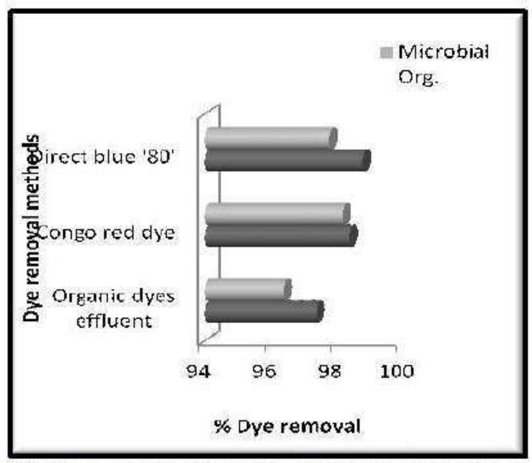

Figure 8. Comparison between microbiological and membrane methods at p = 8 bars, pH = 8.5, T = 27°C

TABLE 1. THE CHARACTERISTICS OF NANOFILTER (NF) AND REVERSE OSMOSIS (RO) MEMBRANES (Source: www.membranes.com)

Types of membrane	Nanofilter	Reverse osmosis
Model	ESNA1-LF2-4040	ESPA-4040
Material	Composite polyamide	Composite polyamide
Module	Spiral wound	Spiral wound
Size (LD* Length) (inch)	inch (4 x 40)	inch (4 x 40)
Active Area, m2	7.9	7.9
Manufacture	Hydranautics	Hydranautics
Max. Feed Water turbidity (NTU)	1	1
Max. Feed Water SDI (15 min)	5	5
Max. Operating Temperature, ºC	45	45
Max. Applied Pressure, bar	21.5	42.1
Feed Water pH Range	3 - 10	2 - 7

TABLE 2. ANALYSIS OF WASTEWATER EFFLUENT FROM THE AFRICAN TEXTILE COMPANY

Parameter	Units	Measured Value during the test (2009)
PH		5-9
TDS	mg/L	450-1000
Conductivity	µs/cm	600-1200
Range of Dye Conc.*	mg/L	20-50

TABLE 3. PHYSICOCHEMICAL ANALYSIS FOR TAP WATER USED IN MEMBRANE TESTING SYSTEM

Parameter	Units	Measured Value During the Test (2009)	WHO Drinking Water Guideline (2009)
PH		7.4 - 8.2	6.5 - 8.5
TDS	mg/L	800 - 2000	1000
Turbidity	NTU	5	5
T. Hardness	mg/L	590 - 1500	500
Electric. Conductivity	µs/cm	1400 - 3700	
Sodium (Na)	mg/L	90 - 240	300
Magnesium (Mg)	mg/L	57 - 160	50
Chloride (Cl)	mg/L	270 - 900	250
Potassium (K)	mg/L	26 - 40	
Calcium (Ca)	mg/L	88-220	50
Sulphate (SO4)	mg/L	90 - 240	250
Bicarbonate	mg/L	177 - 230	
Turbidity	NTU	1 - 2	1.4
SDI		0.4 - 0.6	0.5

TABLE 4. STATISTICAL ANALYSIS OF FITTING THE EXPERIMENTAL DATA FOR NF SYSTEM

Type of dye effluent	Objective response	a_o	a1	a2	a3	a4	Correlation factor (R)	Variance (v)
Organic dyes effluent	Dye removal	72.5332	0.0534	0.0842	0.0459	-0.0003	0.987	0.952

TABLE 5. STATISTICAL ANALYSIS OF FITTING THE EXPERIMENTAL DATA FOR RO SYSTEM

Type of dye effluent	Objective response	a0	a1	a2	a3	a4	Correlation factor (R)	Variance (v)
Organic dyes effluent	Dye removal	69.4327	0.0723	0.1974	0.0421	-0.0059	0.925	0.963

Conclusion

Based on the results obtained, the following conclusions can be drawn: the NF and RO membranes used was remarkably efficient kits for removing dyes substance from effluent wastewater of African Textiles Industry in Kano, Nigeria. Dye removal from wastewater was positively associated to applied pressure, pH, TDS and dye concentration in feed solution, but it was inversely related to feed temperature. Applied pressure and solution temperature have positive impact on NF and RO membranes. But it was inversely related to dye concentration and pH. In this experiment it was confirmed that wastewater with organic dyes effluent treated by NF or RO membranes result in lower rejection and higher permeates flux than wastewater with reactive dyes. It was found that the order of effect of the operating variables on dye removal of NF and RO membranes was in the following sequence: C > pH > P > TDS. At the same operating conditions, one could get from NF system twice the permeated environmental accepted water flow rate and about 50 % less electric power instead of RO membranes. The reduction of electric power came directly from the reduction of the operating pressure of the unit with NF membrane. Results indicated that the use of NF membrane in dye removal from wastewater of the African Textile Company Kano is promising and can be used with higher efficiency, instead of the current microbiological method, which is too slow and time consuming.

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References

Abid, M. F., Zablouk, M. A., and Abid-Alameer, A. M. (2012). Experimental study of dye removal from industrial wastewater by membrane technologies of reverse osmosis and nanofiltration. *Iranian journal of environmental health science & engineering*, *9*(17), 1 - 9.

Afzali, A., Maghsoodlou, S., and Noroozi, B. (2016). Nanoporous Polymer/Carbon Nanotube Membrane Filtration: The "How-To" Guide to Computational Methods. *Analytical Chemistry from Laboratory to Process Line*, 99.

Akbari, A., Remigy, J. C., and Aptel, P. (2002). Treatment of textile dye effluent using a polyamide-based nanofiltration membrane. *Chemical Engineering and Processing: Process Intensification*, *41*(7), 601-609.

Akbari, H. R., Mehrabadi, A. R., and Torabian, A. (2010). Determination of nanofiltration efficency in arsenic removal from drinking water. *Iranian Journal of Environmental Health Science & Engineering*, *7*(3), 273.

Al-Aseeri, M., Bu-Ali, Q., Haji, S., and Al-Bastaki, N. (2007). Removal of Acid Red and sodium chloride mixtures from aqueous solutions using nanofiltration. *Desalination*, *206*(1), 407-413.

Al-Aseeri, M., Bu-Ali, Q., Haji, S., and Al-Bastaki, N. (2007). Removal of Acid Red and sodium chloride mixtures from aqueous solutions using nanofiltration. *Desalination*, *206*(1), 407-413.

Ali, N., and Mohammad, A. W. (2004). Theoretical analysis on interacting effect of steric and Donnan factors in nanofiltration membrane separation system. *Journal Teknologi UTM*, *41*, 41-48.

Avlonitis, S. A., Poulios, I., Sotiriou, D., Pappas, M., and Moutesidis, K. (2008). Simulated cotton dye effluents treatment and reuse by nanofiltration. *Desalination*, *221*(1), 259-267.

AWWA (1992). Membrane Technology Research Committee: Committee Report: Membrane processes in potable water treatment: AWWA, 59.

Bellona, C., Drewes, J. E., Xu, P., and Amy, G. (2004). Factors affecting the rejection of organic solutes during NF/RO treatment-a literature review. *Water research*, *38*(12), 2795-2809.

Bohdziewicz, J., Bodzek, M., and Wąsik, E. (1999). The application of reverse osmosis and nanofiltration to the removal of nitrates from groundwater. *Desalination*, *121*(2), 139-147.

Bohonak, D. M., and Zydney, A. L. (2005). Compaction and permeability effects with virus filtration membranes. *Journal of membrane science*, *254*(1), 71-79.

Brandhuber, P and Amy, G. (1998). Alternative methods for membrane filtration of arsenic from drinking water. *Desalination*, *117*(1), 1-10.

Cadotte, J. E., Petersen, R. J., Larson, R. E., and Erickson, E. E. (1980). A new thin-film composite seawater reverse osmosis membrane. *Desalination*, *32*, 25-31.

Carmen, Z., and Daniela, S. (2012). Textile organic dyes–characteristics, polluting effects and separation/elimination procedures from industrial effluents–a critical overview. In *Organic Pollutants Ten Years after the Stockholm Convention-Environmental and Analytical Update* (pp. 55-81). InTech: Croatia.

Cristiane N, Jose Carlos C, Humberto G: Color and COD Retention by Nanofiltration Membranes. Desalination 2005, 172:77–83.

Gholami, M. I. T. R. A., Nasseri, S. I. M. M. I. N., Alizadehfard, M. R., and Mesdaghinia, A. L. I. R. E. Z. A. (2003). Textile dye removal by membrane technology and biological oxidation. *Water quality research journal of Canada*, *38*(2), 379-391.

Gholami, M., Nasseri, S., Fard, M. A., Mesdaghinia, A., Vaezi, F., Mahvi, A., and Naddaffi, K. (2001). Dye removal from effluents of textile industries by ISO9888 method and membrane technology. *Iranian Journal of Public Health*, *30*(1-2), 73-80.

Gozálvez-Zafrilla, J. M., Sanz-Escribano, D., Lora-García, J., and Hidalgo, M. L. (2008). Nanofiltration of secondary effluent for wastewater reuse in the textile industry. *Desalination*, *222*(1), 272-279.

Holkar, C. R., Jadhav, A. J., Pinjari, D. V., Mahamuni, N. M., and Pandit, A. B. (2016). A critical review on textile wastewater treatments: Possible approaches. *Journal of Environmental Management*, *182*, 351-366.

Hubbe, M. A., Metts, J. R., Hermosilla, D., Blanco, M. A., Yerushalmi, L., Haghighat, F., Lindholm-Lehto, P., Khodaparast, Z., Kamali, M, and Elliott, A. (2016). Wastewater treatment and reclamation: A review of pulp and paper industry practices and opportunities. *BioResources*, *11*(3), 7953-8091.

Ismail, A. F., and Lau, W. J. (2008). The effects of structural and electrical properties of hollow fiber nanofiltration membranes on salt and dye removal under different solution properties. *Jurnal Teknologi*, *49*, 103-113.

Kim, Tak-Hyun, Yuri Lee, Jeongmok Yang, Byunghwan Lee, Chulhwan Park, and Sangyong Kim. "Decolorization of dye solutions by a membrane bioreactor (MBR) using white-rot fungi." *Desalination* 168 (2004): 287-293.

Koyuncu, I. (2002). Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: effects of feed concentration and cross flow velocity. *Desalination*, *143*(3), 243-253.

Kucera, J. (2015). Reverse osmosis: design, processes, and applications for engineers. John Wiley & Sons.

Li, N. N., Fane, A. G., Ho, W. W., and Matsuura, T. (2011). Advanced membrane technology and applications. John Wiley & Sons.

Lopes, C. N., Petrus, J. C. C., & Riella, H. G. (2005). Color and COD retention by nanofiltration membranes. *Desalination*, *172*(1), 77-83.

Molinari, R., Lavorato, C., and Argurio, P. (2016). Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review. *Catalysis Today*.

Nilsson M, Lipnizki F, Ostergren K: Performance, energy and cost evaluation of a nanofiltration plant operated at elevated temperatures. Sep Purif Technol 2008, 60:36–45.

Oller, I., Malato, S., and Sánchez-Pérez, J. (2011). Combination of advanced oxidation processes and biological treatments for wastewater decontamination - a review. *Science of the total environment*, *409*(20), 4141-4166.

Patnaik, P. (2007). A comprehensive guide to the hazardous properties of chemical substances. John Wiley & Sons.

Pereira, A. A. M. (2007). Characterization of polymeric membranes for non-aqueous separations. Eindhoven: PhD Thesis, Eindhoven University of Technology.

Ribera Simon, G. (2013). Technical and environmental viability of membrane technologies in water treatment: NF in drinking water process and MBR for watewater reuse.

Robinson, T., McMullan, G., Marchant, R., and Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource technology*, *77*(3), 247-255.

Salahi, A., Mohammadi, T., Rekabdar, F., and Mahdavi, H. (2010). Reverse osmosis of refinery oily wastewater effluents. *Iranian Journal of Environmental Health Science & Engineering*, *7*(5), 413.

Suteu, D., Zaharia, C., and Blaga, A. C. (2012). Biosorption–current bioprocess for wastewater treatment. *Current Topics, Concepts and Research Priorities in Environmental Chemistry (I), Al. I. Cuza'Universitary Publishing House, Iasi, Romania*, 221-244.

Trotman, E. R. (1984). Dyeing and chemical technology of textile fibres. Wiley.

Visvanathan, C., Marsono, B. D., and Basu, B. (1998). Removal of THMP by nanofiltration: effects of interference parameters. *Water Research*, *32*(12), 3527-3538.

Yao, L., Zhang, L., Wang, R., Chou, S., & Dong, Z. (2016). A new integrated approach for dye removal from wastewater by polyoxometalates functionalized membranes. *Journal of hazardous materials*, *301*, 462-470.

Yu, J., Mao, J., Yuan, G., Satija, S., Jiang, Z., Chen, W., and Tirrell, M. (2016). Structure of Polyelectrolyte Brushes in the Presence of Multivalent Counterions. *Macromolecules*, *49*(15), 5609-5617.