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Reclamation of Aqueous Solution Synthetically Polluted With Endocrine Disturbing Chemicals by Commercial NF Membrane

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Abstract

The target of this study is the removal of Di butyl phthalate, Bisphenol – A and Paracetamol as endocrine disrupting chemicals from aqueous solution using NF99 as a commercial nanofiltration membrane at different operating parameters of pressures (10, 20 and 30 bar), pH (3-11) and different EDCs concentrations using % TOC removal as indicator for the efficiency of the understudied membrane. It was found that the % TOC rejection of Paracetamol was the highest (86 %) at pH 10. The endocrine disrupting chemicals rejection was detected to be increased with the increase of operating pressure till 20 bar. The impact of pH on %TOC removal of EDCs was altered depending on the pka of each compound. Moreover, the anti-fouling property of NF 99 membrane has been investigated by evaluating the membrane rejection and flux using humic acid as a common natural organic matter. The experimental design was estimated by MINITAB software and the results was analyzed by the factorial analysis which suggest that the pH is the most significant factor affecting the removal process.

Keywords: Endocrine Disturping Chemicals, NF99 Membrane, Dibutyl phthalate, Bisphenol a, paracetamol, design factor

1. Introduction

The endocrine disrupting chemicals (EDCs) are acquainted with externally developed compounds that can mutate the job of endocrine order causing hazardous effects for human beings, or their offspring [1]. Lately, proves have been raised that some widely used chemical substances that can reach water sources may infiltrate the endocrine order causing real disturbance [2]. As an instance, bisphenol – A (BPA) which is utilized in numerous industries such as bottle industry, toys and medical equipment [3]. While, dibutyl phthalate (DBP) is exceedingly utilized in some industries such as plastic, cosmetic and surface coating [4]. On the other hand, N-acetyl-4-aminophenol commercially known as Paracetamol (APAP) is contained in medicine to patronize fever and pain [5]. EDCs elimination from drinking water sources is rare due to their very limited concentrations as well as the discomfiture in the analysis [6].Conventional treatment is not fit for EDCs removal. Accordingly, secondary advanced treatment is required such as ozonation, advanced oxidation technologies and/or membrane technologies [7-8]. Accordingly, conventional treatment can be substituted by specialized membranes used for eradication of low molecular weight micro-pollutants such as EDCs [1, 9]. Dead end, as well as cross – flow modes, has been studied recently for removal of EDCs by UF, NF and RO [10 – 15]. Several types of membranes can be used in removal of micropollutants according to the pore size of the membrane as well as the molecular size of the understudied micropollutants [16].Comparing the pore size of various membranes with molecular size of the under examined EDCs, as appeared in Table (1), guides us to use NF or RO membrane in that study. Since RO is used for water desalination and due

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to lower applied pressure NF was elected to eliminate the pre-mentioned EDCs. NF is, a type of membrane that extends the distance between UF and RO, mostly has a non – porous structure accordingly separation takes place through sorption – diffusion mechanization. Diffusion rate has opposite correlation with the size of components causing easier diffusion for smaller components than that of larger ones [6].

2. Experimental

2.1: Materials and methods

The used materials, APAP, BPA and DBP, were of a very high purity bought from Sigma Aldrich. They are used without any further purification. Information about the understudied materials are shown in table (2). Pure ortho phosphoric acid and sodium hydroxide used for pH adjustment were of high purity and provided from Merck Co.

2.2. Experimental setup

The membrane testing cell used is showed in Fig (1). Piston Feed pump used was CatPumps GmbH The maximum produced pressure model 1051 A94013 with 100 bar and 2160 l/h maximum obtained pressure and flow rate respectively. Feed pump is connected to two separate membrane chambers. The flow of both membranes can be collected or analyzed separately. The unit is designed to have a concentrate flow rate ≅ feed flow rate. The design of the experiment was based on MINITAB software, and the analysis of results was conducted by factorial analysis.

2. 3. Design of experiment

The experimental design was performed using Minitab 18 software, the low and the high levels of each factor in addition to the matrix of the full factorial design with %TOC results and fits were represented. All the statistical data of the factorial design analysis were analysed using ANOVA software.

2.4. Properties of membrane used

Thin film composite NF-99 membrane was used during these experiments. The properties of the used membrane are mentioned in table (3).

2.5. Calculation of cross flow velocity

Various cross flow velocities can be obtained among the membranes used so average membrane velocities are calculated from continuity equation (1)

$$\upsilon_c = \Sigma \frac{\upsilon_{c,i} . a_i}{A} \qquad \text{Equation (1)}$$

Where

$\upsilon_c = average\ cross - flow\ velocity$

$A = Total\ Membrane\ surface\ area$

$a_i = increased\ area\ step$

$\upsilon_{c,i} = calculated\ cross - flow\ velocity\ on\ the\ increased\ area$

Cross-flow velocity and dimensions of the used membrane are demonstrated in Fig (2) and the corresponding cross-flow velocities for different flow rates are represented in table (4).

Table (1): properties of different membrane types.

Membrane types	Different membrane characteristics		
	Applied pressure	Permeate flux range (l/(m².h.bar))	Pore size (nm)
Microfiltration	0.1 – 2 bar	> 50	> 100
Ultrafiltration	< 5 bar	10 – 50	5 – 100
Nanofiltration	3 – 15 bar	1.4 – 12	0.5 – 5
Reverse Osmosis	7 – 100 bar	0.05 – 4	0.1 – 1

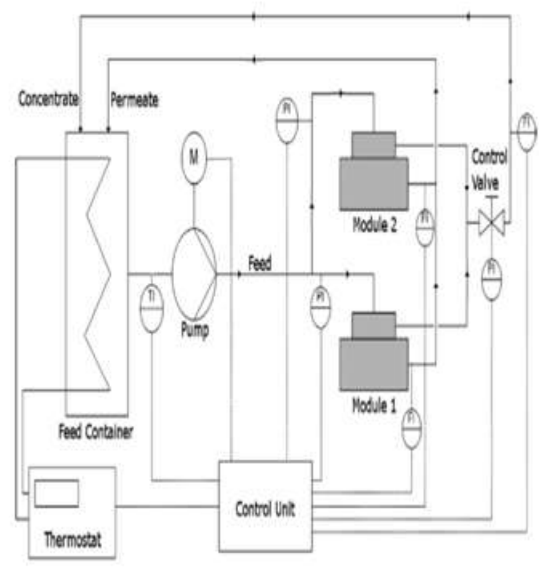


Fig (1): Schematic diagram of the membrane test unit used in experimental setup

Table (2): Structures of the studied EDCs and molecular properties of studied EDCs.

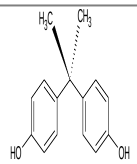
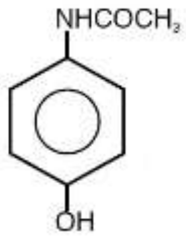
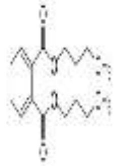
Properties	Bisphenol - A	Paracetamol	Di butyl phthalate
Structure			
Molecular formula	$C_{15}H_{16}O_2$	$C_8H_9NO_2$	$C_{16}H_{22}O_4$
IUPAC name	4,4'-(propane-2,2-diyl) diphenol	N-acetyl-*p*-aminophenol	Dibutyl phthalate
Pka	9.59 - 11.3	9.5	4.8
Molecular size (Å)^3	221.36	138.08	274.34
Polar surface area (Å)^2	40.46	49.33	52.60
Length (Å)	12.39	11.29	13.98

Table (3): Main characteristics of the membranes used in the experimental test module

Parameter	Unit	NF-99
Supported material	-	Polypiperazine
Maximum operating pressure	10^5(N/m2)	55
$MgSO_4$ rejection	%	≥98
pH range	-	3-11
Maximum temperature	°C	50
Molecular weight cutoff	Da	200

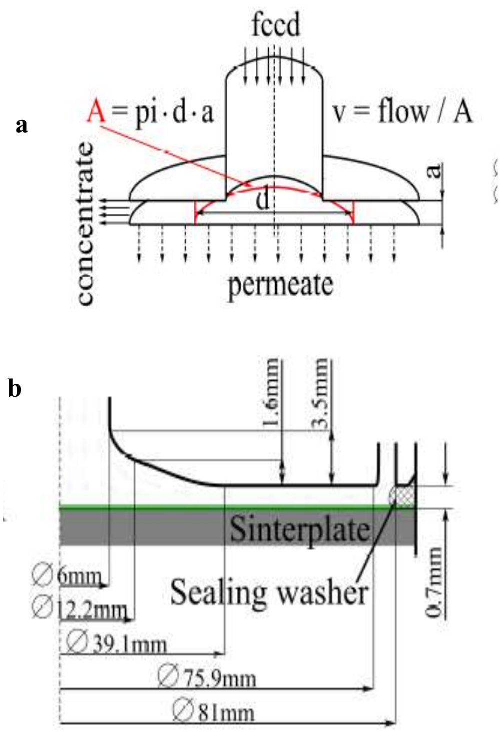


Fig (2) a: Outlines for the calculations of cross-flow velocity, b - Dimensions of the used membrane

Table (4): Calculated cross-flow velocities for corresponding flow rates

Flow rate (L/h)	**Cross-flow velocity (m/s)**	$J_{Stabilized}$ ($m^3/m^2/s$)
500	0.60	1.07×10^{-4}
1000	1.10	3.17×10^{-5}
1500	1.70	1.33×10^{-5}

2.6. Analysis

Total organic carbon TOC was measured with a TOC analyzer (Torch -Teledyne Tekmar) with accuracy of 99.9%. TOC was used for degradation of the under studied pollutants.

3. Results and discussion

3.1. Optimizing operating conditions

In the beginning, several parameters, feed pressure, pH of the solution and the concentration of the understudied substrates, were adjusted to obtain the most effective setup for the experiments.

3.1.1. Influence of pressure

Variable feed pressures, between 10-30 bar, were studied and the percent removals of the understudied EDCs were calculated to select the highest removal compared with the most suitable feed pressure. The results in Fig (3) showed that% TOC removal increased with feed pressure increasing between (10 – 20 bar) then slight decrease was observed afterword indicating that 20 bar feed pressure can be considered the optimum feed pressure. Also, the order of the understudied EDCs was APAP > BPA > DBP which in accordance with the length of each molecule and its corresponding size as mentioned in Table (1). In addition to the size exclusion, the Donnan effect resulting from the electrostatic interaction between the membrane (NF 99) and the charged solutes (EDCs) are governing the solute transport that will be explained explicitly in the effect of pH in the next section [17 -18].

3.1.2. The effect of pH on the EDCs removal:

The polyamide membranes have been manifested that the % rejection varied with the pH of feed solution, this can be attributed to the ionisable groups in the membrane structure [19] or to the EDCs molecule dissociation. In order to study the impact of EDCs solution pH, several experiments at different pH were conducted. Fig. (4) Shows that the influence of pH on % TOC removal of the studied EDCs in pH range of 3-11 under 20 bar feed pressure.

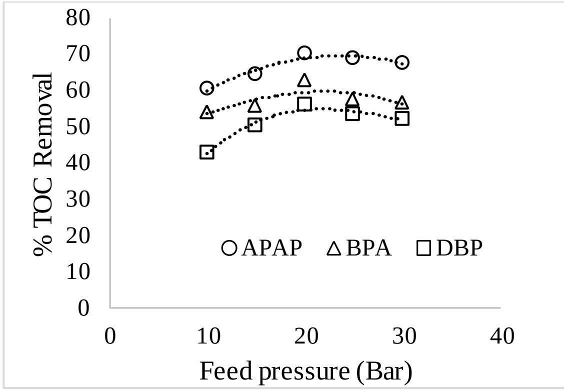


Fig (3): the %TOC removal of the studied EDCs at different feed pressures

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At pH ≤ 5 the rejection of DBP decreases with the increase of the pH and at pH ≥ 7, the rejection is increased with increasing the pH value while, lower rejection has been recognized between pH 5-7 with insignificant effect of pH at this range [20].

Meanwhile, at pH ≤ 7 the rejections of APAP and BPA decrease with the increase of the pH and at pH ≥ 9, their rejections are increased with increasing the pH value while, lower rejection has been recognized between pH 7-9 with insignificant effect of pH at this range [21].

This may be linked to the dissociation equilibrium pKa values the understudied EDCs which 5 for DBP and 9 for APAP and BPA. Since most of dissociated organic compounds exists in a negatively aionic form at pH more than pKa and protonated positively charged ions at pH less than pKa. [22].

NF 99 membrane is positive at pH 3 - 7 [18] and at pH < pKa, the understudied EDCs are positively charged due to the protonation of the aromatic ring donating repulsive forces. At pH ≥ 7 in case of DBP and at pH ≥ 9 in case of APAP and BPA repulsion occur between negatively charged membrane and negatively charged EDCs is attributed to hydrolysis of the carboxylic or hydroxyl groups. At higher pH the pole size of the membrane change larger the rejection of EDCs slightly decreased [23].In the overlap area (5-7 for DBP and 7-9 for APAP and BPA), there is attraction forces between positively charged EDCs and the negatively charged membrane resulting lower rejection.

3.1.3. Effect of the presence of Humic acid

An extreme defect for NF membrane implementation is the Anti-fouling property owing to the fact of its tight pores. The fouling of NF membranes modifies the membrane features and have an impact on the removal of the pollutants. Natural organic matter (NOM) is the main creator for membrane fouling [24, 25]. The extent of membrane fouling can be marked out by the decline in the normalized permeate flux and the percent rejection in presence of (NOM). To investigate the extent of fouling caused by the existence of the humic acid (HA) as one of widespread (NOM) on the % TOC removal of EDCs, two sets of experiments were conducted. Firstly, the % TOC removal of EDCs was measured before and after the filtration of a 5 mg/L of HA separately. The second set is filtering the solution of EDCs (40 mg/l of BPA + 5 mg/l HA, 100 mg/l of APAP + 5 mg/l HA and 80 mg/l of DBP + 5 mg/l HA) Fig. 5 a, b, c manifested the % TOC removal of EDCs by NF 99 membrane as function of volume filtered at 20 Bar at pH (7).

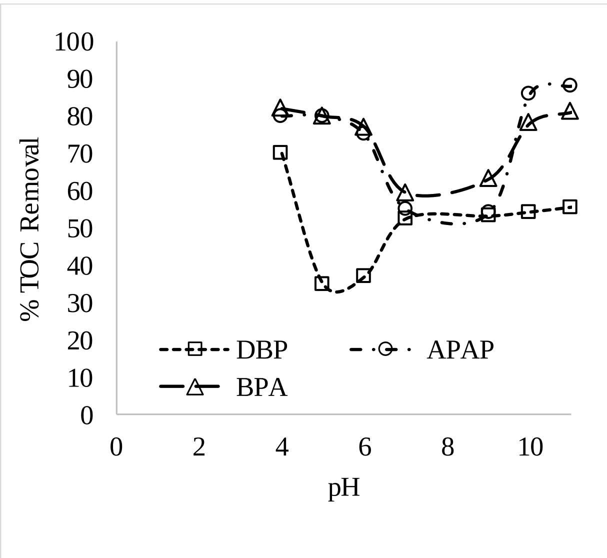

Fig (4): the effect of pH on %TOC removal of EDCs

The second set is filtering the solution of EDCs (40 mg/l of BPA + 5 mg/l HA, 100 mg/l of APAP + 5 mg/l HA and 80 mg/l of DBP + 5 mg/l HA) Fig. 5 a, b, c manifested the % TOC removal of EDCs by NF 99 membrane as function of volume filtered at 20 Bar at pH (7). It is observed that in presence of HA decreases in % TOC over the first 600 mL filtered compared with % TOC obtained in the absence of HA. This behaviour can be reasoned to the adsorption sites of the membrane surface being partially occupied by HA molecules and inselectivity of the membrane towards EDCs and HA causing a lower filtered volume [26]. Moreover, fouling diminished the surface charge of membrane and subsequently lowering the electrostatic repulsions between the fouled membrane and the EDCs leading to decline in the % TOC removal [27, 28]. Moreover, the solution of ECDs and HA are filtrated for measuring the change in permeate flux as an indicator of membrane fouling. . A slight flux decline (30% in J_{stab} of ECDs) occurred immediately after HA was introduced to the feed solution as observed in Fig 6 a, b and c the NF99 shows good resistance to fouling by HA at 20 bar applied. This behaviour is in consent to previous studies [29, 30].

3.1.4. Effect of feed EDCs concentration

To investigate the effect of EDCs concentration on %TOC removal, 80, 90, 100, 110 and 120 mg/l DBP solutions at pH 5 (Fig.7 a), 60, 70, 80, 90 and 100 mg/l BPA solutions at pH 10 (Fig.7 b) and 20, 30, 40, 50 and 60 mg/l APAP solutions at pH 10 (Fig.7 c) were filtered at 10, 20 and 30 bar. The results represented in Fig 7 demonstrated that % TOC removal slightly diminished as the concentration of EDCs augmented at different pressures. This conduct can be ascribed to the molecular feature of EDCs such as acidity, solubility, capability to form hydrogen bonding, etc. This phenomenon may be help EDCs adsorption in the membrane which deform the active layer pore in case of excess pressure, leading to low rejection values [31-33].
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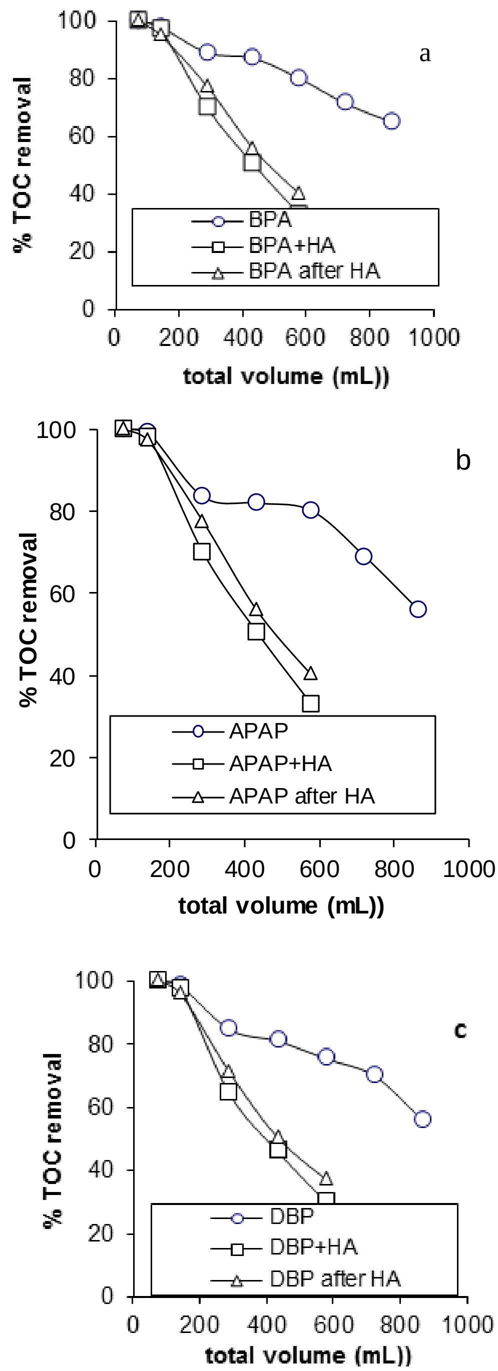

Fig. (5): Effect of HA (5mg/l) on %TOC removal of a) of BPA (40 mg/l), b) APAP 100 mg/l and c) and DBP 80 mg/l at 20 Bar feed pressure

3.1.5. Experimental design

The % TOC removal, results performed of APAP that has the highest % TOC removal of the understudied EDCs using NF 99 are shown in Table 5. Factorial design conducted utilizing MINITAB [34]. The achieved results were analyzed by factorial analysis (FA), using ANOVA analysis to determine the significant factors and their interactions that can be affected the rejection of APAP using NF99.

The Model F-value of 29.90 implies that the model is significant. Since, there is only 0.01% chance for this F-value to occur due to the noise. P-values < 0.0500, indicating that the model terms are significant. In this case A, B, C are significant model terms. Values Greater than 0.1000 indicate the model terms are not significant. The **Predicted R^2** of 0.8157 is in reasonable agreement with the **Adjusted R^2** of 0.8874; i.e. the difference is < 0.2 **A_{deq} Precision** measures the signal to noise ratio. Adequate signal is found in this experimental design since the signal to noise ratio is 15.218 since, a ratio > 4 is desirable).

Final Equation in Terms of Coded Factors:

S_{qrt} (% TOC Removal) = 7.94+ 0.4765 Feed pressure - 0.5796 APAP concentration+1.15pH

The equation in terms of coded factors is used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Table 6 manifested the summary of the investigation of variance (ANOVA), which declared the significance of the operating parameters and their interaction impacts based on the p-value (at 0.1 level of significance). The p-values show that pH is the main significant effects on the rejection of APAP, as the p-value was 0.0005.

The Pareto chart generated by MINITAB software, is shown in Fig. 8. The effect of pH in feed solution for the rejection of APAP was found to be significant. Meanwhile, the effect of feed pressure and APAP concentration was found to be less significant. Fig (9) shows 3D plot of the interaction of feed pressure and pH on the %TOC removal conducted on APAP using NF99

The square root transformation was performed and box-cox plot for power transform is shown in Fig 10

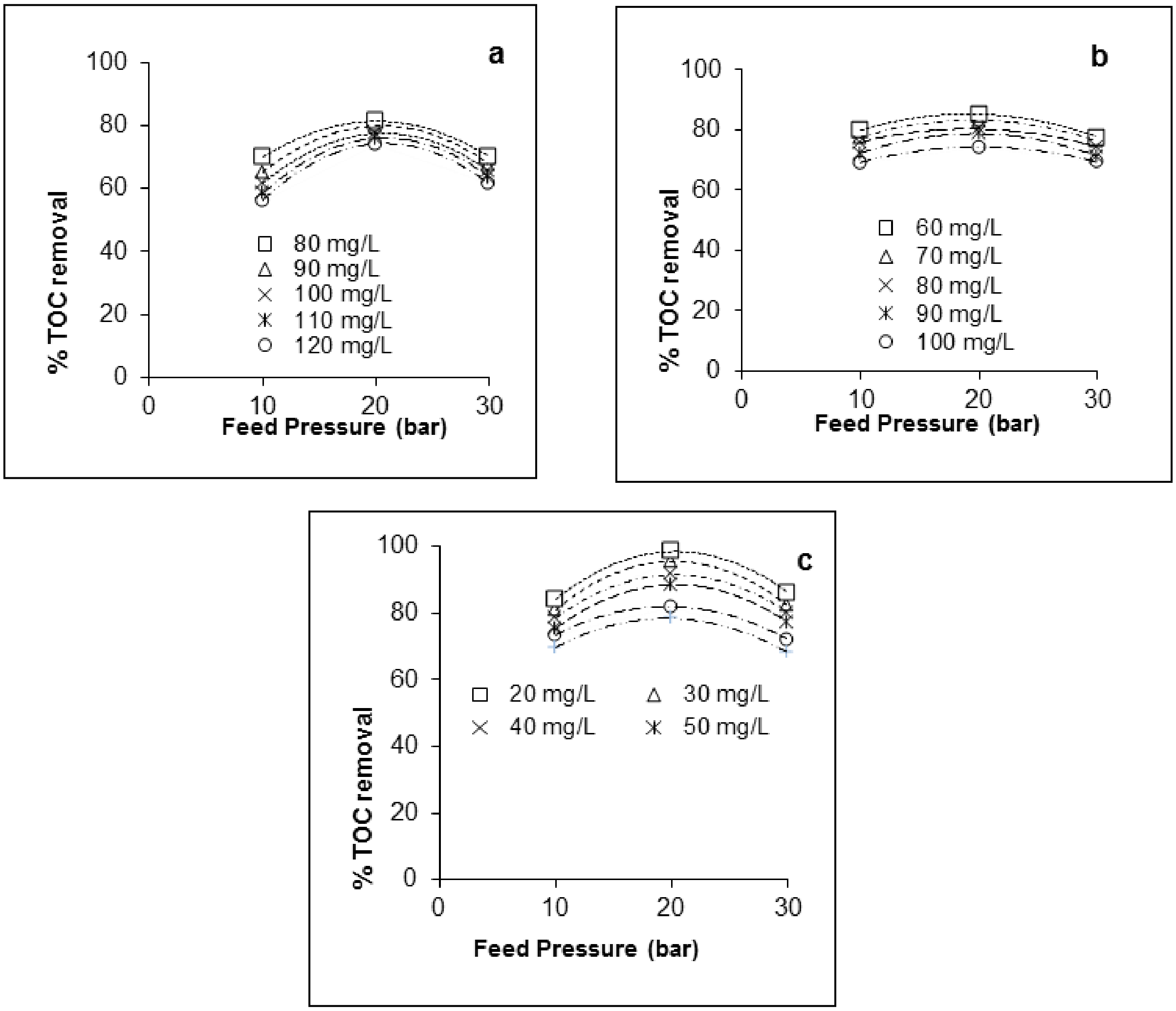

Fig (7): the effect of feed EDCs concentration on % TOC removal of EDCs

Table (5): Experimental results of % TOC removal for APAP using NF99:

		Factor 1	**Factor 2**	**Factor 3**	**Response 1**
Std	Run	A:Feed pressure	B:APAP concentration	C:pH	% TOC Removal
8	1	20	100	4	41.2
4	2	10	100	4	33.7
3	3	20	20	10	98.4
10	4	10	100	10	69.7
7	5	20	20	4	81
11	6	20	20	10	98.4
9	7	20	100	10	78.3
12	8	10	20	4	43.1
6	9	10	20	4	43.1
2	10	10	100	10	69.7
1	11	20	100	4	41.2
5	12	10	20	10	84.17

Table 6: ANOVA analysis for selected factorial model at Square Root transformation of the rejection of APAP using NF99

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	22.60	3	7.53	29.90	0.0001	significant
A-Feed pressure	2.73	1	2.73	10.82	0.0110	significant
B-APAP concentration	4.03	1	4.03	16.00	0.0039	significant
C-pH	15.84	1	15.84	62.87	< 0.0001	significant
Residual	2.02	8	0.2519			
Lack of Fit	2.02	4	0.5039			
Pure Error	0.0000	4	0.0000			
Cor Total	24.61	11				

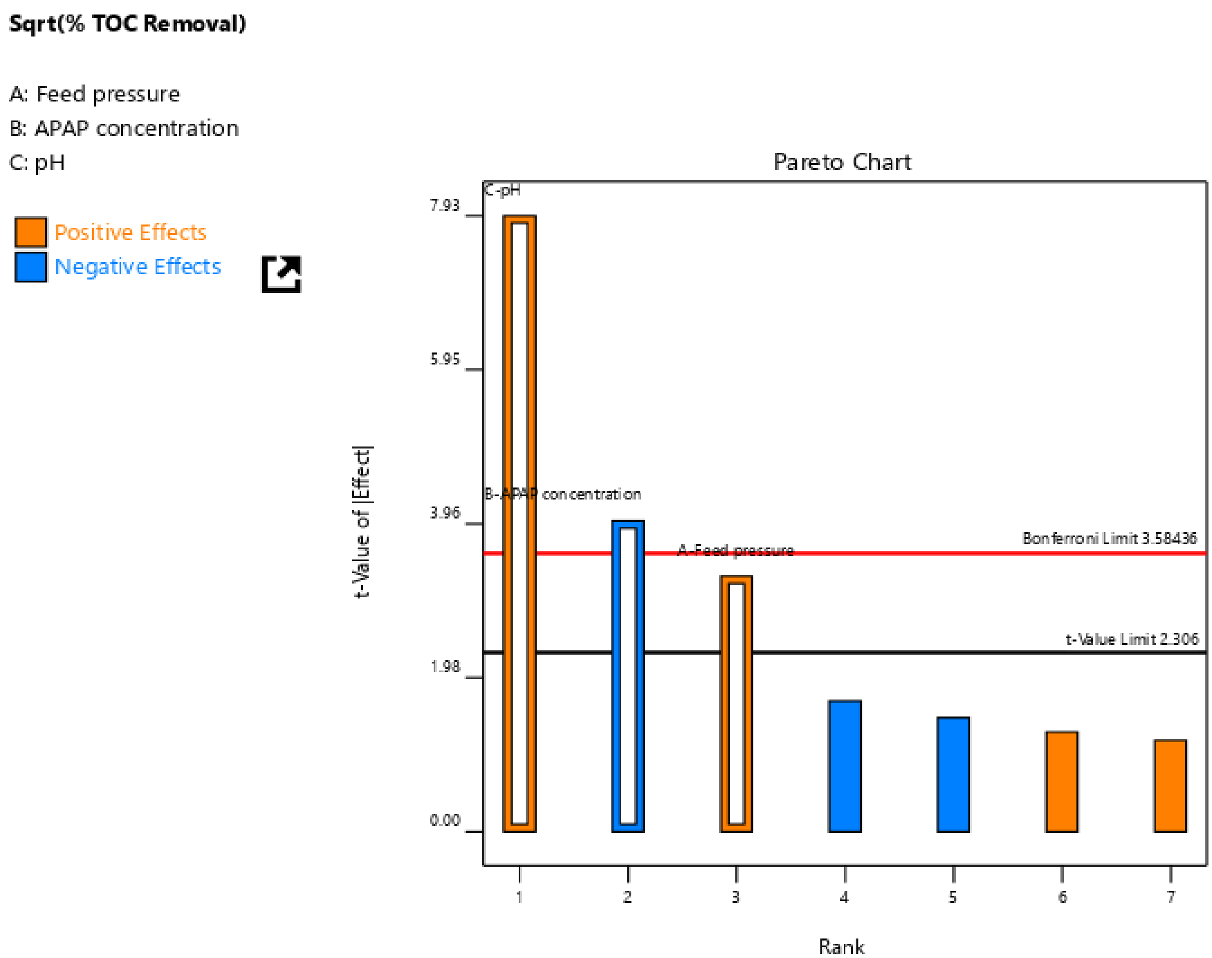

Fig. (8): The Pareto chart for the %TOC removal conducted on APAP using NF99

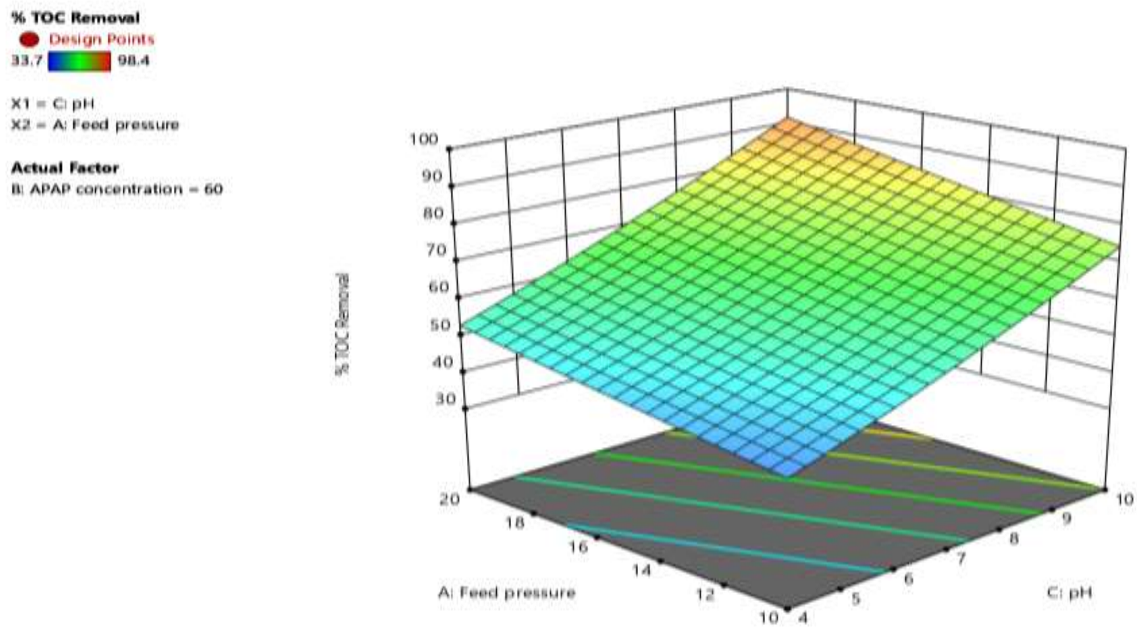

Fig (9): 3D plot of the interaction of feed pressure and pH on the %TOC removal conducted on APAP using NF99

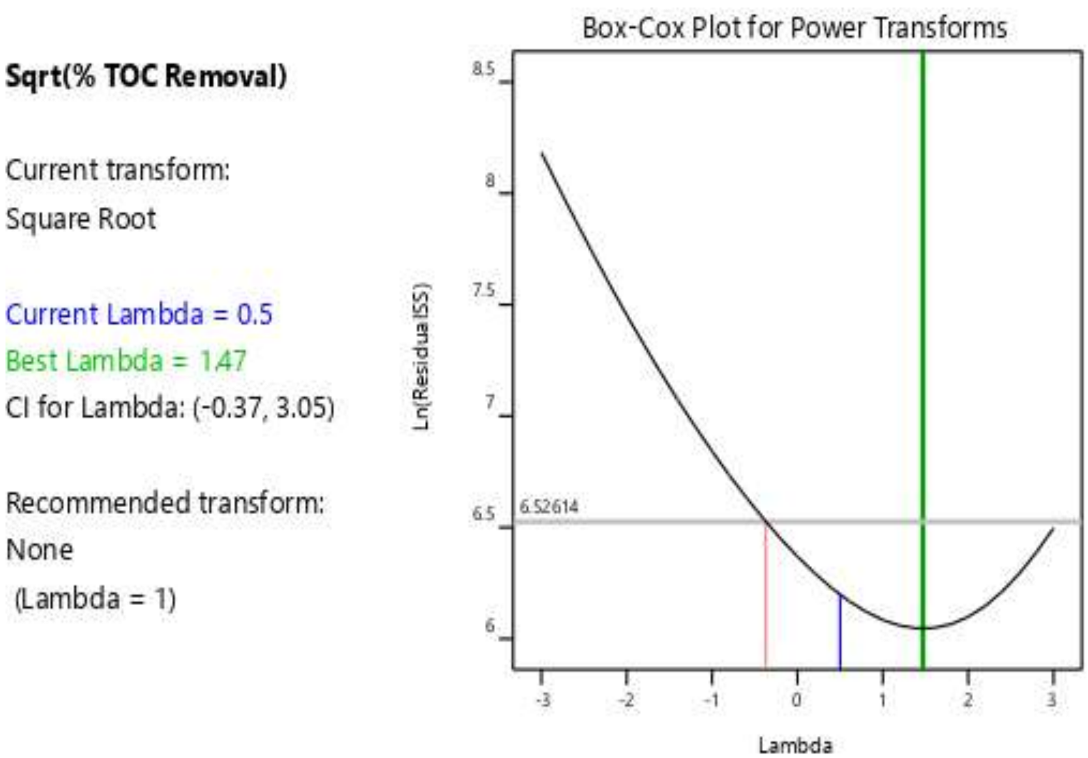

Fig.(10): box-cox plot for power transform

4. Conclusions

The commercial NF99 membrane has been used in a laboratory-scale study to investigate its performance in the removal of EDCs at different pressures, feed concentrations and pH values, using permeate flux and rejection as representative parameters. It was found that NF 99 is capable of efficient removal of EDCs achieved 70, 80 and 86 % TOC removal of DBP, BPA and APAP respectively at feed pressure 20 bar. Moreover, anti-fouling property of NF 99 membrane was conducted using humic acid as a common natural organic matter which concluded that a slight decrease around 30% in J_{stab} of ECDs is observed. This indicated that NF99 shows good resistance to fouling by HA at 20 bar applied pressure and this fouling due HA adsorption onto the membrane surface which lead to the decline in water permeability. The experiment design was performed using MINITAB software and the ANOVA analysis of APAP removal using NF99 results was conducted which indicated that pH is the most significant factor affects the removal process. The Pareto chart for the %TOC removal conducted on APAP using NF99 showed that the effect of pH in feed solution for the rejection of APAP was found to be significant. Meanwhile, the effect of feed pressure and APAP concentration were found to less significant.

5. Conflicts of interest

"There are no conflicts to declare".

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