

Humic acid removal from water using a novel fabricated antifouling carbon nanotube bucky - paper membrane and effect of operating parameters

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Abstract

In present work, a novel supported bucky paper (BP) membrane was fabricated and evaluated for humic acid (HA) removal from water. For better understanding the effect of operating variables, response surface methodology (RSM) was also applied. Three independent parameters namely TOC concentration (5, 10 and 15 mg l⁻¹), operating time (10, 20 and 30 min) and transmembrane pressure (TMP) (1, 2 and 3 bar) were selected for TOC removal (%) and permeate flux analysis.

The results revealed that the membrane could effectively remove HA primarily through electrostatic repulsion and then adsorption mechanisms. The study also showed that about 65% and 35% of the removed HA were through repulsion and adsorption mechanisms respectively. Based on analysis of variance (ANOVA), it was showed that the effect of TMP was strongly significant on the removal and flux (P-value <0.05). In addition, statistical test confirmed that RSM based on the Box–Behnken was a suitable method for optimizing the main operating variables for HA rejection using BP membrane (R²=0.97). At optimum condition (TMP of 1.5 bar, TOC concentration of 12.7 mg l⁻¹) and operating time of 13.5 min, removal obtained 67.4% and the flux was 233.4 l m⁻²h⁻¹.

In general, the synthesized BP membrane showed a relatively good rejection of HA and revealed antifouling properties over the filtration time.

Keywords: Filtration, natural organic matter; carbon nanotubes, response surface methodology, Box- Behnken

1. Introduction

Natural organic matter (NOM) is defined as complex mixture of organic materials entering to natural watercourse from decay products of plants and animals (Crittenden *et al.*, 2012; Sillanpää, 2015). NOM content varies in different waters. It can be in the range of 1 to 20 mg/L (as total organic carbon (TOC)) in surface waters (Crittenden *et al.*, 2012). From health significance point, NOM can react with free chlorine and form carcinogenic disinfection by products (DBPs) in drinking water. Moreover, NOM significantly affect the various water quality parameters and treatment processes. It can complex with metals and some hazard organic chemicals (e.g. pesticides), making the consequent problems. Furthermore, NOM affect the necessity for and application of water treatment chemicals (coagulants and disinfectants) so that increase the required doses to obtain effective performance (Crittenden *et al.*, 2012). Therefore, NOM removal from waters is a challenging topic, and an efficient treatment process is required. Different technologies with varying degrees of success have been proposed for NOM removal include coagulation and flocculation, electrocoagulation, ion exchange, adsorption, membrane technology, and advanced oxidation processes (Jafari *et al.*, 2015; Mahvi *et al.*, 2009; Mahvi *et al.*, 2011; Moussavi *et al.*, 2014; Rezaee *et al.*, 2014; Sillanpää, 2015).

Membrane technology, as an environmentally friendly and effective option, has increasingly been regarded for different pollutants removal from water. Commonly reverse osmosis (RO) and nanofiltration (NF) membranes are used for water desalination and softening. NOM mixtures can also be efficiently removed via these high pressure membranes (Zazouli *et al.*, 2008). In recent decade low-pressure membranes such as ultrafiltration (UF) has proven to be a reliable and promising method for

water treatment. However, UF membrane has some drawbacks. The most common drawback with UF membrane for NOM removal is membrane fouling. NOM can adsorb to membranes, obstruct the membrane pores and lead to a rapid decline in water permeability through the membrane (Crittenden *et al.*, 2012; Zazouli *et al.*, 2010). Therefore, NOM removal by UF membrane with less problem and higher efficiency has been considered by many researchers (Jafari *et al.*, 2015; Song *et al.*, 2011).

In recent years various nanomaterials have been widely applied for water and wastewater treatment aspects especially for novel membranes fabrication and modification (Dumée *et al.*, 2011; Jafari *et al.*, 2015; Rezaee *et al.*, 2015). Accordingly Carbon nanotube (CNT) as a dramatic product of nanotechnology has been used for new type of membrane synthesis and application (Dumée *et al.*, 2011; Gilani *et al.*, 2013; Vatanpour *et al.*, 2011).

Bucky paper (BP), a new type of membranes, is a very easy made and flexible thin sheet of functionalized CNTs which stand together after vacuum filtration. BP has been made and applied for different purposes due to its unique characteristics (Cooper *et al.*, 2003; Do *et al.*, 2011; Dumée *et al.*, 2010; Sears *et al.*, 2010; Sweetman *et al.*, 2013). Accordingly, it can effectively be used for water purification because of its flexibility and high pollutants removal. Dumée *et al.* fabricated a BP membrane and successfully investigated for distillation (Dumée *et al.*, 2011). It was also reported that a fabricated BP with pore size of ~41 nm could remove humic acid (HA) in a dead end operation system (Yang *et al.*, 2013). Furthermore it was very effective in removal of biological agents such as *Escherichia coli* from water (Sweetman *et al.*, 2013).

The BP characteristics depend on some variables such as CNTs types (single walled or multi walled), synthesis procedure, CNT loading in the dispersion, applied vacuum or pressure and solvent type (Li and Kröger, 2012; Muramatsu *et al.*, 2005; Smajda *et al.*, 2007; Zhang *et al.*, 2014).

Unmodified CNTs do not remain in suspension state in a solvent and settle down after a while. In addition they agglomerate in combination with polymers for matrix membrane synthesis. This problem can be solved through surfactants addition or functionalization. In functionalization of CNTs using mixture of nitric acid and sulfuric acid, carboxyl and hydroxyl groups are induced which improve the dispersion and enhance the tensile strength of the fabricated BP. (Xu *et al.*, 2008; Zhang *et al.*, 2014).

BP fabrication is conducted using vacuum filtration of about 1 bar (Smajda *et al.*, 2007) or pressurized method of 1 to 12 bar (Zhang *et al.*, 2014). High pressures decrease the porosity of the BP due to the flexibility of the spongy CNT network structure (Zhang *et al.*, 2014).

BP has generally been fabricated as free standing membranes in which the fabricated membrane peeled off and use after filtering the CNT suspension through a filter. However in this work, a novel supported bucky-paper was fabricated and used for humic acid (HA) rejection. Design

of experiments (DOE) method was also applied for this study as a known method in response surface methodology (RSM) (Çoruh and Elevli, 2015; Jafari *et al.*, 2014; Rezaee *et al.*, 2014). For this purpose, three main variables in terms of transmembrane pressure (TMP), humic acid concentration and filtration time with three levels were employed.

The aim of this work is to evaluate a fabricated BP membrane for NOM rejection and analysis the role of operating parameters on the performance of the membrane.

2. Materials and methods

2.1. Membrane synthesis and characterization

In this study multi-walled carbon nanotube (MWCNTs) (purity of 95% and outer diameter of 10–50 nm and length of 10 µm) was purchased from Petroleum Research Centre (Iran). Functionalization process was performed according to the method described by Naghizadeh *et al.*, using a mixture of sulfuric and nitric acids (3:1 V/V) to obtain functionalized CNT (Naghizadeh *et al.*, 2013). Certain amount of functionalized CNTs (0.2 g) was placed in 100 ml of ethanol with certain amount of ethyl acetate (0.02 g) as polymeric binder under sonicating (30 kHz for 1 h) at room temperature (~25 °C) to gain a uniform dispersion. The certain volume of this suspension was then taken and vacuumed using a vacuum pump (~0.6 bar) through a non-woven polyester substrate filter (150 µm thickness and mean pore diameter of 10 µm). Then it was allowed to dry in an oven at 40 °C for 24 h. Synthesized BP was then characterized and employed for HA removal.

2.2. Membrane characterization

Membrane surface and cross section morphology were analyzed via field emission scanning electron microscopy (FESEM) (Hitachi-S4160). Further analysis of membrane pores and structure was conducted using an image analyzer software (Abramoff *et al.*, 2004).

Water contact angle (CA) as an important factor for membrane hydrophilicity was determined using the conventional sessile drop method (Data physics, OCA 15 plus). Contact angles small amount of deionized water (4 µL) on the surface of BP membrane were determined at room temperature. The mean value of at least five water droplets was presented as the result of this measurement.

The porosity of the BP was analyzed using N₂ adsorption/desorption using an ASAP-2010 porosimeter (Micromeritics Corporation GA) and the specific surface area of the BP was calculated using the Brunauer–Emmett–Teller (BET) method.

2.3. Membrane flux

Membrane flux (J) (lm²h⁻¹) was measured using the following equation

$$J = \left(\frac{V}{A \cdot t} \right) \quad (1)$$

Where V (L) is the volume of permeate water, t denotes for operating time (h) and A_m (m^2) stands for effective surface area of membrane.

2.4. Experimental set up

The digital photograph of applied set up for this study is shown in Fig. 1. The main parts of the set up were: a 2-L feed (storage) tank, a low-pressure pump, membrane cell (9.6 cm^2 of effective surface area), flow meters, gauges and valves. Temperature control system was also applied to maintain the temperature of feed solution at $24 \pm 1^\circ\text{C}$. For process analysis the synthetic the pump was turned on to flow the solution the to the membrane cell. At different interval times filtered water was collected for analysis and the concentrate was continuously returned to the storage (feed) tank.

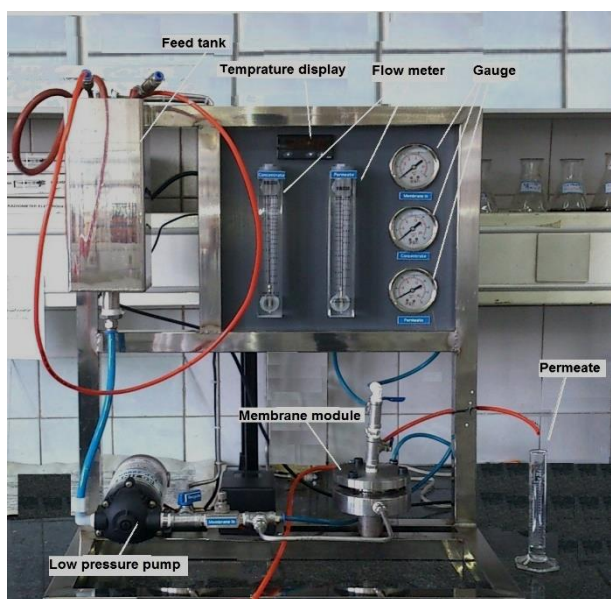


Figure 1. Set up experiment

2.5. NOM model solution and analysis

In this study, NOM model solution was synthetically prepared by dissolved humic acid (HA) (Acros organics company, NJ USA) in distilled water. In this study NOM concentration was analyzed using a TOC analyzer (TOC-VCPH, Shimadzu Japan).

The removal percentage was calculated from the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

Where R refers to rejection, C_p is the TOC concentration of permeate and C_f is the TOC concentration of feed. The adsorbed fraction was calculated using the following mass balance equation in a condition that the concentrate was recycled to feed tank for 60 min.

$$M_{ads}(\%) = \frac{C_f V_f - [C_t V_t + \sum C_p V_p] \times 100}{C_f V_f} \quad (3)$$

Where, M_{ads} is the portion of adsorbed TOC per effective membrane area, C_f , C_t and C_p are the concentrations of TOC in feed tank at the beginning, the concentrations of TOC in feed tank at the end of filtration and concentration of TOC in permeate, respectively. Differences between Eq. (21) and Eq. (3) reveal the repulsed TOC fraction.

2.6. Experiments design

In order to obtain the effect of different operating parameters on performance of the membrane, response surface methodology (RSM) was employed. For this aim, Box- Behnken method with three main variables and three levels was used for filtration modelling and optimization. Main variables (and the related levels) include applied pressure (1, 2 and 3 bar), initial TOC concentration (5, 10 and 15 mg l^{-1}) and operating time (10, 20 and 30 min). Table 1 presents the experimental design and related results of the experiment runs for the responses (flux and HA rejection).

In this study, other conditions such as pH and temperature kept constant and a new membrane was used for each run of experiments and the runs were carried out based on randomized order by Design Expert software (trial version 7.0).

3. Results and discussion

3.1. Membrane characteristics

Digital photograph of the fabricated BP is shown in Fig. 2. The fabricated supported membrane was enough flexible and can be folded and cut with scissors. As displayed in the image, the white margin reveals the supported nonwoven fabric and the place of sealing O-ring of vacuum system.

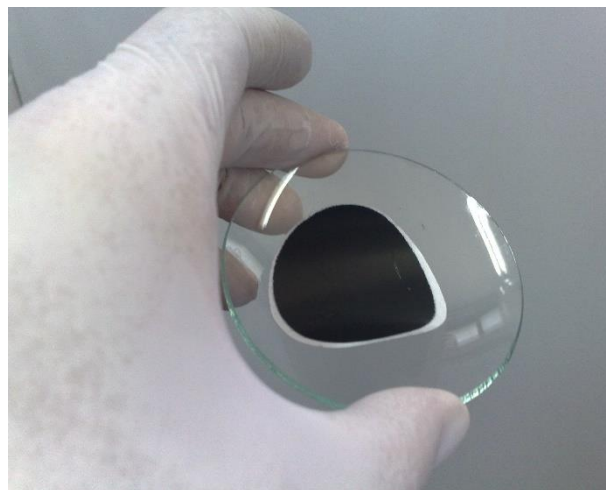


Figure 2. Digital photograph of the BP membrane

Figs. 3 and 4 depict the surface and cross section microphotograph of BP respectively. As shown, CNTs have formed a network like structure on the surface and in nonwoven substrate. Since the CNTs penetrated in porous structure of non-woven substrate, created a porous network and enhanced the mechanical strength of the membrane.

The mean of surface pore diameter of the membrane from FESM image was 30 ± 13 nm. This value of diameters is in the range of a typical UF membrane. In spite of common polymeric membranes, the size and morphology of BPs vary considerably depend on the fabrication process. From our analysis, the shape of the pores is not typical and a wide range of size distribution exists. As previously noted, some parameters such as dispersion quality and specially CNTs properties including length, diameter, functionalization method and pressure condition can affect BP pores characteristics (Li and Kröger, 2012; Muramatsu *et al.*, 2005; Smajda *et al.*, 2007; Zhang *et al.*, 2014). Normally, CNTs with smaller length and lower content develop small pore sizes (Li and Kröger, 2012) which is an important variable for pollutants rejection via membrane size exclusion.

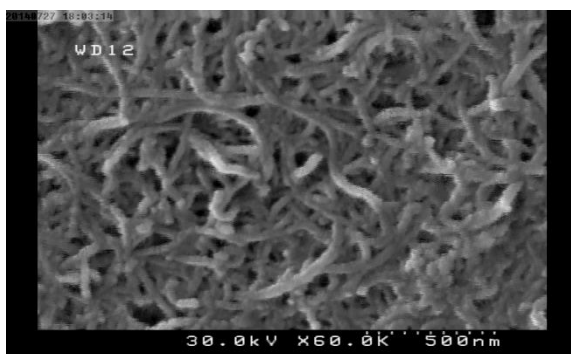


Figure 3. FESEM image of top surface BP

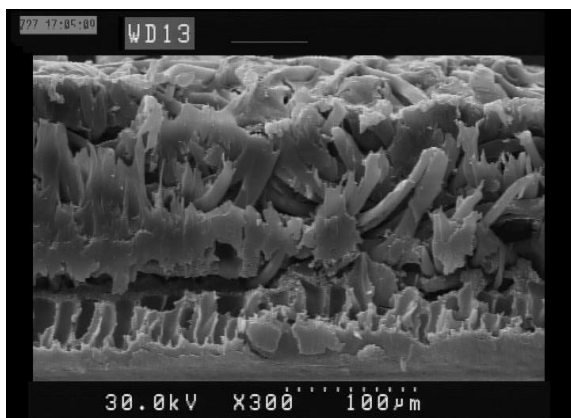


Figure 4. Cross sectional FESEM image of BP on non woven substrate

Fig. 5 depicts the CA of the prepared membrane. CA for synthesized membrane was $45\pm3^\circ$. Generally, the smaller CA represents higher hydrophilicity. From Fig. 5, static attachment of water droplet on the top surface of the membrane indicates the great hydrophilic property of the membrane. Although, pristine (non-functionalized) CNTs are hydrophobic in nature, it is well known that introducing hydroxyl (-OH) and carboxylic (-OOH) functional groups can change the tendency of the membrane to be wet, improve the hydrophilicity and enhance the membrane flux (Yin *et al.*, 2013).

The overall porosity of the BP membrane was calculated about 70%. The porosity of BP membrane is primarily affected by CNTs type, length, CNT loading, preparation condition and sonication time (Li and Kröger, 2012; Yang *et al.*, 2013). Different range of porosity from 30% to 90% have been reported based on different experiments (Cranford and Buehler, 2010). For example, it was reported that CNTs with higher length built higher porosity (Li and Kröger, 2012) and lower loaded CNTs developed lower porosity (Li and Kröger, 2012). Generally porosity incorporated with other properties of the membrane such as hydrophilicity is a key factor for membrane performance in terms of flux and antifouling properties (Zhao *et al.*, 2013).

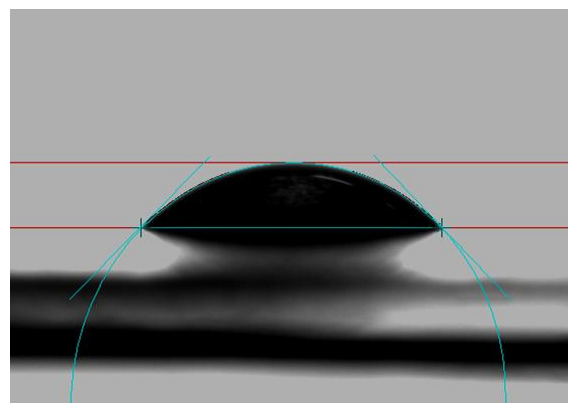


Figure 5. Water contact angle image of the BP

BET surface area of the membrane was calculated about $231 \text{ m}^2/\text{g}$. In general, different surface areas related to CNTs could be obtained under different experimental conditions. CNTs surface area can change through modification and blending with other chemicals. After a functionalization process the surface area of pristine CNT can increase from $130 \text{ m}^2/\text{g}$ to $171 \text{ m}^2/\text{g}$ (Naghizadeh *et al.*, 2013). However, in membrane process surface area is crucial parameter. Higher surface areas of the membrane can provide higher adsorptive or repulsive sites on the membrane that could improve the membrane performance. Hence, higher surface area with negatively charge could be of interest for rejection of substances with the same charge.

3.2. Membrane pure water flux

The measured pure water flux (J_0) for synthesized membrane was $300\pm15 \text{ l m}^{-2}\text{h}^{-1}$. The pure water flux of a membrane is mainly a function of pore size. However, other factors affect the flux. In this regard, membrane hydrophilicity is an important factor as previously noted. Furthermore, membrane thickness, compaction and inner properties are important too. The overall thickness of the membrane was measured about $250\pm30 \text{ μm}$ for the synthesized membrane. Amount of CNTs applied for bucky paper preparation and vacuum pressure could affect the membrane thickness, pores and porosity. Generally higher thickness resulted from higher loaded CNTs, prevents water transport across the membrane due to reduction in porosity and blocking the substrate pores.

3.3. Effect of main parameters on the rejection and flux

As shown in Fig. 6 at the beginning of filtration, the rejection occurred primarily by a combination of both adsorption and repulsion. At the starting of filtration, feed TOC of 4.6 mg l⁻¹ reduced to 1.32 mg l⁻¹ in permeate. Meanwhile TOC slightly increased in concentrate and feed. Although this change is not significant, it shows that at up to 30 min of filtration, the rejection is occurred by both adsorption and repulsion. After exhausting the adsorption capacity, the rejection proceeds by charge repulsion and the permeate curve stands nearly constant. In other word, increase in the feed solution, due to recycling of concentrate, do not affect the membrane rejection performance.

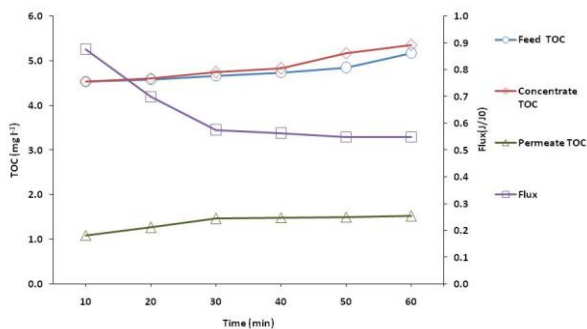


Figure 6. Trend of different elements at filtration of HA in a loop experiment. (Initial TOC=4.6 mg l⁻¹, pH≈7.5, TMP= 2 bar)

Fig. 7 shows the different portions of TOC mass calculated by Eq. (2). With regard to Fig.7, about 56.6% of HA is rejected by charge repulsion and about 30% is adsorbed by the membrane. These results showed that functionalized CNTs could change the removal mechanism from adsorption to repulsion. From the figure as there are several adsorbing sites on the CNTs, HA is rapidly adsorbed on the sites and after a while, removal is mainly happened through electrostatic repulsion (Fig. 6). In other hand, the

Table 1. The results experimental randomized runs for HA rejection and the related flux

Run No	A:TMP (Bar)	B:TOC (mg l ⁻¹)	C:Time (min)	Flux (lm ² h ⁻¹)	Rejection (%)
1	3	15	20	228.1	45.0
2	1	5	20	165.6	84.7
3	2	10	20	296.9	63.3
4	2	5	30	202.1	65.0
5	3	10	10	375.0	29.5
6	2	10	20	275.0	61.0
7	1	15	20	109.4	69.4
8	2	5	10	312.5	64.9
9	1	10	10	187.5	75.0
10	2	15	30	163.5	57.0
11	1	10	30	164.6	74.0
12	2	15	10	250.0	61.2
13	3	5	20	281.3	50.0
14	2	10	20	285.9	63.5
15	3	10	30	166.7	47.0

flux declined rapidly at first 30 min of operation (Fig. 6) due to adsorption of HA on the surface and into the pores of BP. However, based on normalized permeate flux ratio (J/J_0) during the filtration time (Fig. 6, right vertical axis), about 40 % of flux decline happened in first 30 min, after that a slow slope is seen. Nevertheless, the flux does not decrease more than 45% after 60 min of operation. Such behaviour can be due to gradually adsorption of HA in membrane pores and increasing of feed TOC due to retentate recirculating to the feed flow. Although UF modification, process alteration and integrated processes have been reported to enhance the UF membrane performance in term of flux decline (Liu *et al.*, 2011; Song *et al.*, 2011), in BP the decline rate is not as rapid as commercial UF membranes (Song *et al.*, 2011). Functionalized (carboxylated) CNTs effectively reject HA substances and hinder the fouling due to induce negatively charges on membrane surface which effectively improve both the rejection and antifouling property. This is mainly happened through increasing the electrostatic interaction between membrane charge and HA (Song *et al.*, 2011).

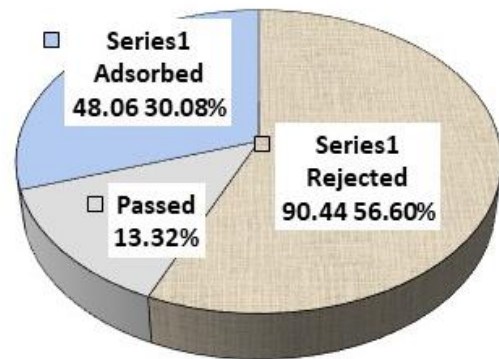


Figure 7. Different portions (repulsed, passed and adsorbed) of HA through filtration by synthesized BP membrane.

Driving force can also affect the membrane performance in terms of rejection and flux decline in different conditions. The effect of TMP versus time and TOC concentration on HA rejection have been illustrated by 3D surface plots (Figs. 8-A and 8-C). As shown, with increase of TMP, the rejection decreased. Statistically, according to ANOVA results (Table 2), TMP is the most important parameter on the rejection (p value < 0.05). Although in some cases it is expected that increase of TMP could form a sieving network by a layer of

particles that retain the smaller particles (Crittenden *et al.*, 2012), but this figure shows that higher TMP may create a path for penetrating small molecules or particles. Moreover, flexible structure of BP may be affected by high driving force. From Fig. 8-D and 8-E, increase of flux as a function of TMP increment can be seen, but the increase is not linear. Based on ANOVA results (Table 2) the effect of TMP on the flux is strongly significant (p value < 0.05).

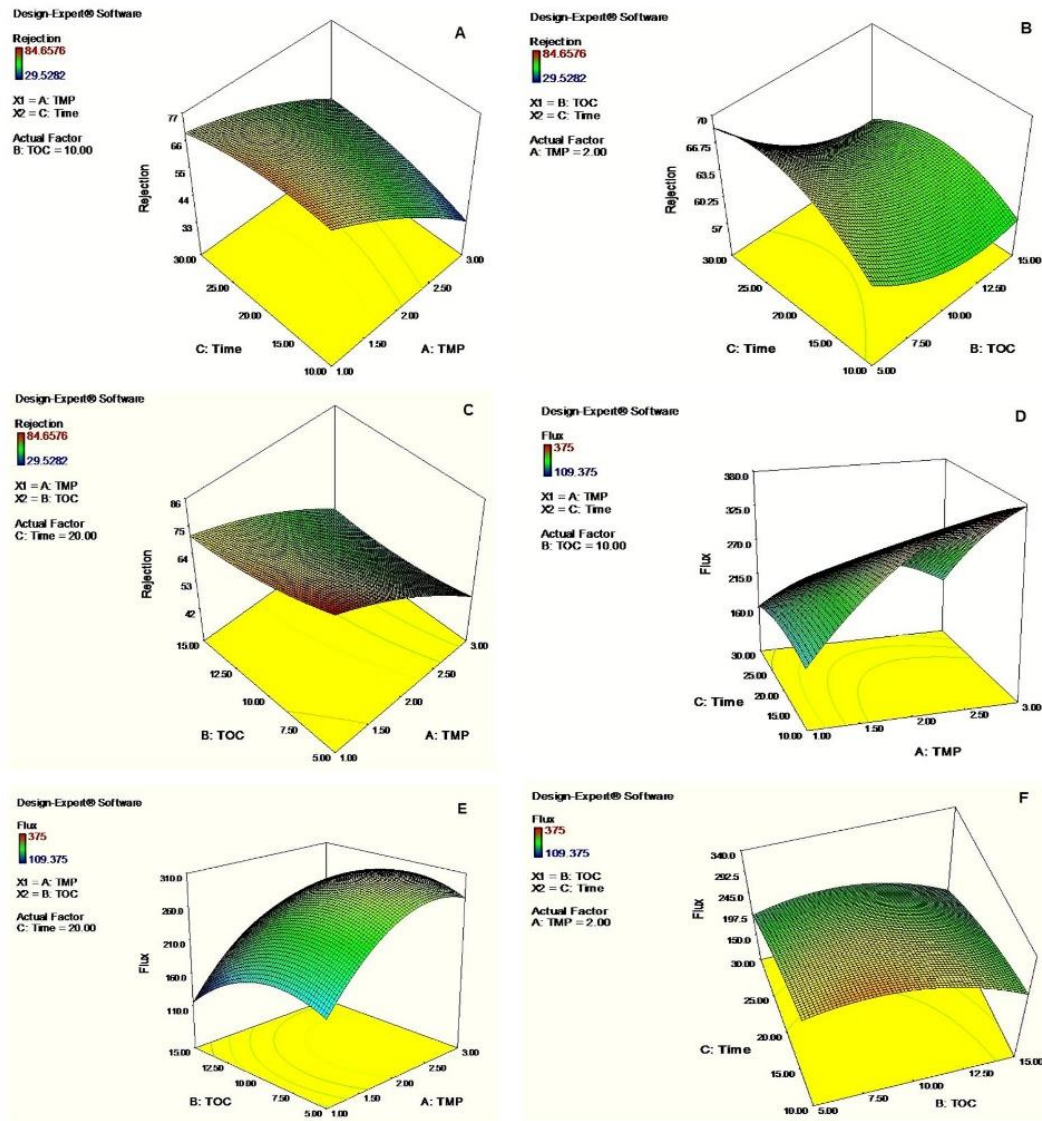


Figure 8. 3D surface plots of variables: (A) rejection as a response of TMP and Time (B) rejection as a response of TOC and Time (C) rejection as a response of TMP and TOC (D) flux as a response of TMP and Time (E) flux as a response of TMP and TOC (F) flux as a response of TOC and Time

Operating time significantly affects the rejection performance (p -value < 0.05), (Table 2). Generally, operating time has a high effect on membrane fouling in case of adsorption of the pollutants by membrane. On the other hand, repulsive mechanism in membrane can increase the membrane lifetime. From Fig. 6 the rate of flux

decline is nearly rapid at the beginning of the filtration. As previously noted, negative charges of hydroxylated groups on the membrane can prevent the fouling and flux decline. Since HA has high affinity to pristine CNTs (Naghizadeh *et al.*, 2013), introducing functional groups on the CNTs could significantly increase the rejection properties.

Accordingly, reduction of adsorption capacity results in reduction of fouling phenomenon.

Furthermore, TOC concentration in the solution affected both the rejection and flux (Fig. 8-B, 8-E and 8-F). Commonly, increase of TOC in the case of TMP increase resulted in accumulation of TOC near the surface of the

membrane and consequent concentration polarization phenomenon. From ANOVA results, (Table 2), TOC is significant for rejection and flux (p-value <0.05). However, increase of TOC may result in reduction of electrostatic charges on the membrane surface and decrease of the charge potential.

Table 2. Analysis of variance (ANOVA) results for flux and rejection of HA

	Flux					Rejection				
	Sum of Squares	df	Mean of Square	F Value	p-value Prob > F	Sum of Squares	df	Mean of Square	F Value	p-value Prob > F
Model	73815.27	9	8201.70	63.44	0.0001	2527.03	9	280.78	15.89	0.0036
A-TMP	22467.58	1	22467.58	173.78	< 0.0001	2161.58	1	2161.58	122.31	0.0001
B-TOC	5534.40	1	5534.40	42.81	0.0012	127.75	1	127.75	7.23	0.0434
C-Time	22911.38	1	22911.38	177.21	< 0.0001	19.27	1	19.27	1.09	0.3442
AB	2.44	1	2.44	0.019	0.8961	26.45	1	26.45	1.50	0.2757
AC	8594.84	1	8594.84	66.48	0.0005	85.30	1	85.30	4.83	0.0794
BC	143.50	1	143.50	1.11	0.3403	4.66	1	4.66	0.26	0.6296
A ²	8944.56	1	8944.56	69.18	0.0004	32.95	1	32.95	1.86	0.2304
B ²	6093.75	1	6093.75	47.13	0.0010	25.82	1	25.82	1.46	0.2808
C ²	651.29	1	651.29	5.04	0.0748	38.54	1	38.54	2.18	0.1998
Residual	646.43	5	129.29			88.36	5	17.67		
Lack of Fit	407.17	3	135.72	1.13	0.5001	84.50	3	28.17	14.59	0.0648
Pure Error	239.26	2	119.63			3.86	2	1.93		

3.4. Model evaluation

Developed models as the coded values for rejection and flux are as follows.

$$\text{Flux (lm}^{-2}\text{h}^{-1}\text{)} = 285.94 + 52.99 \times A - 26.30 \times B - 53.52 C + 0.78 \times A \times B - 46.35 \times A \times C + 5.99 \times B \times C - 49.22 \times A^2 - 40.63 \times B^2 - 13.28 \times C^2 \quad (4)$$

$$\text{Rj (\%)} = +62.60 - 16.44 \times A - 4.00 \times B + 1.55 \times C + 2.57 \times A \times B + 4.62 \times A \times C - 1.08 \times B \times C - 2.99 \times A^2 + 2.64 \times B^2 - 3.23 \times C^2 \quad (5)$$

The built modes were evaluated based on the statistical tools. According to p-values, both the produced models are significant (Table 2). For the models, determination coefficient (R^2) were 0.99 and 0.97 for flux and rejection, respectively and the adjusted R^2 and predicted R^2 are high enough (>0.9) that confirm the validity of produced models for flux and rejection.

Furthermore, p-values of lack of fit (LOF) were 0.5 and 0.064 for flux and rejection respectively. Insignificance of LOF values confirms the validity of the developed model for prediction of a process.

3.5. Optimal condition

Optimum condition for HA rejection and flux was obtained. Based on these conditions at TMP of 1.5 bar, TOC concentration of 12.7 mg l⁻¹ and time of 13.5 min, rejection was 67.4% and the flux was 233.4 lm⁻²h⁻¹. This forecast was evaluated by an extra test at the optimal condition. The rejection was obtained 70 % that was near to that was predicted by the model.

4. Conclusion

The results of this study revealed that functionalized CNT application as BP membrane can effectively reject HA. The antifouling property of the membrane is promising for future application for NOM rejection. This study also revealed a long life operating of the system with less fouling phenomenon due to inducing of hydrophilic functional groups to BP membrane. It was revealed that the

built quadric model can predict the process suitably. Although the membrane has many benefits based on the results of this study, but some challenges still remain including the possible release of nano materials to the finished water. Future studies can focus on the monitoring and possible release of CNT through BP membrane.

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