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Bentazon removal from aqueous solution by reverse osmosis; optimization of effective parameters using response surface methodology

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ABSTRACT

Although bentazon is widely used as an agricultural herbicide, it is harmful to humans and poses many environmental threats. This study focused on the treatment of wastewater contaminated with bentazon pesticides using membrane technology. In this regard, low-pressure reverse osmosis (RO) was employed as it has already been used in the removal of other micro-pollutants. The effects of process variables on water flux and bentazon rejection were studied: temperature, pressure, and bentazon feed concentration. Based on central composite design (CCD), the quadratic model was engaged to correlate the process variables with the water flux and the bentazon removal responses. The obtained results showed that the bentazon rejection increased by enhancing the pressure while it decreased at higher feed solution concentration. However, with increasing temperature, the amount of bentazon removal was reduced. A bentazon rejection efficiency of 100 % could be achieved under optimum conditions (i.e., the temperature of 29.8 °C and hydrostatic pressure of 12.6 bar for a feed solution concentration of 66.9 mg/L). Therefore, reverse osmosis can effectively remove bentazon.

1. Introduction

Nowadays, human beings experience a more comfortable life through industrial, agricultural, and medical advances. However, this better life has been achieved with the price of polluting environmental and natural resources. The disposal of industrial and domestic wastewater into the environment that contaminates our water resources, as well as the constraints of supplying water for industrial, agricultural, and domestic usage, have forced societies to make optimal use of these resources and even their reuse. The main problems with conventional water purification methods are their feasibility for treating pollutants such as pesticides in low concentrations and their resistance toward biological degradation [1,2]. At first glance banning the inflow of pesticides into water sources appear to be the best way to reduce their health and environmental risks. Because of the lack of effective control of entry into water resources, conventional treatment methods such as chemical coagulation, precipitation, disinfection, and adsorption have little effect on the removal of these contaminants [3,4,5]. The efficacy of these methods is influenced by the chemical nature of pesticides. Advanced methods have also been utilized for the degradation of agricultural toxins: ultrasonic waves [6], biodegradation [7], ozonation [8,9], oxidation by anodic Fenton [10], treatment with UV/H_2O_2 [11], and photocatalytic degradation [12,13,14]. However, the drawbacks of the latter methods, such as the complexity of the process, high cost, and high chemical consumption, have prevented their extensive application. The membrane technologies developed in the past five decades could be considered as a suitable alternative to the conventional treatments mentioned above. In this regard, reverse osmosis (RO) and nanofiltration (NF) are two membrane technologies that have been used for the treatment of wastewater contaminated with agricultural toxins [15,16,17]. Bentazon, as a herbicide, has been used for the selective control of broadleaf weeds and sedges in beans, rice, corn, peanuts, and mint [18]. Bentazon is highly soluble in water and presents a strong potential for water resource contamination. According to a report presented by the U.S. Environmental Protection Agency (US-EPA) in 1995, the

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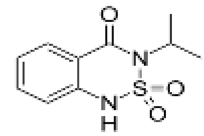
amount of bentazon in groundwater and surface water exceeds levels of concern. Bentazon is defecated by warm-blooded animals without any uptake of residues in edible tissues. Based on its toxicological properties, bentazon is categorized as non-carcinogenic ("Group E") by the US-EPA, and its limit value as a drinking water guideline presented by the WHO was raised to 30 µg/L [19]. Hindin et al. investigated the elimination of various pesticides such as dichloro-diphenyl-trichloroethane (DDT), 1,1-dichloro-2,2-bis(4-chlorophenyl) ethane (TDE), benzene hexachloride (BHC) and lindane by RO using asymmetric cellulose acetate (CA) membrane in the late 60s [16,20]. They found that the RO process with the use of the CA membrane could be a promising process for the production of potable water from the water sources contaminated with harmful organic pesticides. Chian *et al.* also reported the exceptional performance of the RO process in removing various toxins [21]. Over the past two decades, many efforts have been made to utilize RO to remove herbicides, insecticides, fungicides, and pesticides from different sources of water [16,22]. However, the number of studies investigating the removal of bentazon from contaminated waters by RO is scanty. The main aims of this paper are to evaluate the efficiency of the RO process to remove bentazon from wastewater and investigate the role and effect of process variables such as temperature, hydrostatic pressure, and feed solution concentration. A systematic experimental procedure is required to investigate the effect of process variables on the separation of bentazon by RO. The variables usually have some interaction effects; therefore, the design of experiments approach was used to design less-tedious experimental runs to find the optimal values to achieve maximum removal efficiency. The response surface methodology (RSM) statistical method and Design Expert software based on the analysis of variance was used for data analysis.

2. Materials and methods

2.1. Feed solution

The feed solution was made by mixing technical grade bentazon (> 96 %) with ultrapure water that was purchased from the Aria Shimi Co. The characteristics of the bentazon are presented in Table 1.

Table 1. Characteristics of bentazon [23].

IUPAC name	**3-Isopropyl-1H-2, 1, 3-benzothiadiazin-4(3H)-one 2,2-dioxide**
Class	Herbicides
Classification	Benzothiadiazole
Molecular structure	
Chemical formula	$C_{10}H_{12}N_2O_3S$
Molecular weight	240.28
Length (˚A)	11.98
Width (˚A)	7.493
Height (˚A)	8.378
Solubility in water (mg/L)	570

2.2. RO membrane

The flat sheet asymmetric RO membranes used in this investigation were supplied from Dow Film Tec© (for tap water). These polyamide thin-film composite (TFC) membranes with an active layer of cross-linked aromatic polyamide are commercially available membranes, which are usually used for low-pressure RO tests.

2.3. Reverse osmosis system

Figure 1 illustrates a schematic diagram of the bench-scale RO setup with a rectangular stainless steel cross-flow membrane cell, which provides an effective membrane area of 140 cm^2 (10 ×14 cm) with a channel height of 0.4 cm. Mesh spacers were inserted in the feed channel for raising turbulence in the feed stream and mass transport increase in the membrane. Three diaphragm pumps (series KJ-2000 from Deng Yuan Industrial Co., Taiwan) were used to recirculate the feed solution under 1.5 L/min and at an applied pressure range of 3 to 15 bar. A heating/cooling system equipped with a stainless steel heat exchanger coil immersed in the feed solution was used to hold the operating temperature in the range of 20 to 40 °C (±1 °C).

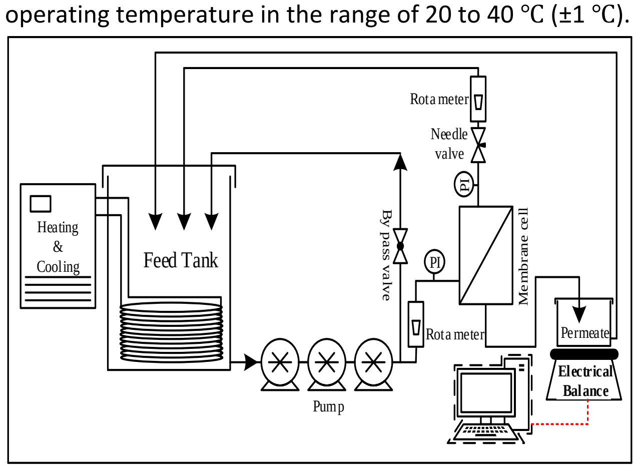


Fig.1. Schematic diagram of the bench-scale reverse osmosis system

The flow rate and pressure of the influent and retentate of the feed solution from the membrane cell were monitored using a rotameter and pressure gauge, respectively. The permeate flow rate was determined by measuring the weight change over a selected time period. The permeate was then returned to the feed tank. The water flux J_w (L/m^2.h; LMH) was calculated as Eq. (1) [24,25]:

$$J_w = \frac{\Delta m}{\rho\, A\, \Delta t} \quad (1)$$

where Δm (g) is the weight change of permeate during each experimental run, A (m^2) is the effective area of the RO membrane, ρ (g/m^3) is the water density, and Δt (h) is the test time. The percent bentazon rejection, R, is then calculated from Eq. (2) [15]:

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

where C_p (mg/L) and C_f (mg/L) are permeate and feed bentazon concentrations, respectively. The C_p was determined by a spectrophotometer and the calibration curve of the bentazon concentration versus its absorbance. The spectrometric measurements for the solutions containing bentazon have been applied in λ_{max}=334 nm, which is the peak absorbance for bentazon.

2.4. Experimental design

Response surface methodology is a set of statistical and mathematical techniques used to create experimental models [26]. The purpose of these designs is to optimize the response, which is affected by several independent variables. Therefore, three factors and five levels of central composite design (CCD) were used to investigate the influence of factors such as temperature, hydrostatic pressure, and feed solution concentration on the treatment of wastewater polluted with bentazon using RO. The water flux and bentazon rejection were used as system responses. The factors and their levels used in RSM with the actual and coded values are shown in Table 2. The experimental design consisted of eight factorial points, six axial points, and center points for each one, leading to collections of experiments. The results obtained by the Design Expert Software (version 10.0, State-Ease, Inc., Minneapolis, MN) were analyzed using analysis of variance (ANOVA).

Table 2. Variable and level of the experimental design

Variables	Symbol	Coded levels				
		-2	**-1**	**0**	**+1**	**+2**
Temperature (°C)	T	20	25	30	35	40
Pressure (bar)	P	3	6	9	12	15
Bentazon concentration (mg/L)	C	50	100	150	200	250

3. Results and discussion

3.1. Mathematical model

Based on the design of the CCD, 20 experiments were carried out to evaluate the effect of the process factors on the responses such as water flux and bentazon rejection. The obtained results are presented in Table 3. To develop an empirical relationship between the responses and the variables of the process, the regression calculation was applied to the obtained CCD data. Various models were evaluated based on the values R^2, adjusted R^2, and predicted R^2. Considering that the values of R2, adj-R2, and pred-R2 for the water flux are 0.9614, 0.9466, and 0.8468 and those of bentazon rejection are 0.9661, 0.9279, and 0.8319, respectively, RSM has suggested a second-order polynomial equation for predicting the effect of the variables on both responses. The final models, in terms of the coded factors for the water flux (Y_1) and bentazon rejection (Y_2), are presented in Eqs. (3) and (4):

$$Y_1 = 24.53 + 1.79 * T + 3.06 * P - 0.26 * C - 0.93 * T.P - 0.65 * T\hat{}2 - 1.57 * P\hat{}2 - 0.39 * C\hat{}2 \quad (3)$$

$$Y_2 = 97.584 + 0.75 * T + 1.48 * P - 1.22 * C - 0.97 * T.C - 0.585 * P.C - 0.388 * P\hat{}2 - 0.687 * C\hat{}2 \quad (4)$$

The analysis of variance (ANOVA) was employed to evaluate the adequacy of the second-order model. The results are summarized in Table 4, in which the high F-value and the p-value less than 0.05 indicate the adequacy of the model as the linear terms, second-order terms, and interaction terms. The results demonstrate very good conformity between real values with values predicted by the model. Based on the ANOVA result, the model for water flux and bentazon rejection was well-fitted to the experimental data by the p-value of <0.0001 for both responses and the model F-value of 46.37 and 25.32, respectively. The lack of fit is non-significant (i.e., greater than 0.05), which represents the validity of the quadratic model for both responses. The water flux with six terms, namely the linear terms of temperature (T) and pressure (P); the second-order terms of temperature (T^2), pressure (P^2), and bentazon concentration (C^2); and the interaction term of temperature * pressure (TP), were significant in the design range with the p-values of <0.0001, <0.0001, 0.003, < 0.0001, 0.04 and 0.0096, respectively. According to Table 4, the bentazon rejection equation has seven terms, including the linear terms of temperature, pressure, and bentazon concentration; the second-order terms of pressure (P^2) and bentazon concentration (C^2); and the interaction terms of pressure * bentazon concentration (PC) and temperature * bentazon concentration (TC), with the p-values of 0.008, <0.0001, < 0.0001, 0.0046, 0.0001, 0.0257, and 0.0019, respectively.

Table 3. Experimental CCD matrix and experimental results

Trial	Factors			Y_1 (water flux)		Y_2 (bentazon rejection)	
	T	P	C	experimental	calculated	experimental	calculated
1	30	9	250	23.21	23.49	92.36	97.27
2	30	9	150	24.84	24.53	97.90	97.58
3	25	12	200	23.38	23.83	96.14	96.10
4	25	12	100	24.57	24.41	97.34	97.77
5	30	9	150	25.53	24.53	97.60	97.58
6	30	9	150	23.55	24.53	97.79	97.58
7	30	9	150	24.49	24.53	97.18	97.58
8	30	15	150	31.20	24.37	99.23	98.99
9	40	9	150	26.03	25.51	91.83	99.71
10	35	6	100	21.46	21.81	96.90	97.08
11	30	9	50	23.57	23.49	97.45	97.27
12	35	12	100	26.25	26.47	98.47	99.93
13	30	9	150	24.84	24.53	98.35	97.58
14	30	9	150	24.75	24.53	96.82	97.58
15	35	6	200	20.39	21.35	94.16	93.87
16	30	3	150	12.94	12.13	92.97	93.07
17	20	9	150	18.66	18.35	96.85	96.71
18	25	6	100	15.52	16.03	94.67	94.56
19	25	6	200	15.66	16.25	95.10	95.23
20	35	12	200	24.91	25.21	96.34	96.58

Table 4. Analysis of variance (ANOVA) for responses of the model

Source	Water flux (L/m².h)		Bentazon rejection (%)	
	F Value	p-value	F Value	p-value
Model	46.37	< 0.0001	25.32	< 0.0001
T-Temperature	79.07	< 0.0001	12.31	0.008
P-pressure	129.31	< 0.0001	113.79	< 0.0001
C-bentazon conc.	1.69	0.2263	77.26	< 0.0001
TP	10.74	0.0096	4.67	0.0626
TC	0.36	0.5649	20.57	0.0019
PC	0.49	0.4998	7.48	0.0257
T^2	16.15	0.003	0.95	0.358
P^2	47.53	< 0.0001	15.09	0.0046
C^2	5.75	0.04	47.25	0.0001
Lack of Fit	2.23	0.2007	0.58	0.6541
PRESS	44.98		9.84	
C.V %	3.6		0.52	
R-Squared	0.9614		0.9661	
Adj R-Squared	0.9466		0.9279	
Pred R-Squared	0.8468		0.8319	

A comparison of the RSM model prediction given in Eqs. (3) and (4) and the experimental results are presented in Figure 2. It is observed that the RSM model prediction is best fitted to the experimental results. Figure 2 validates the performance of the second-order polynomial equation.

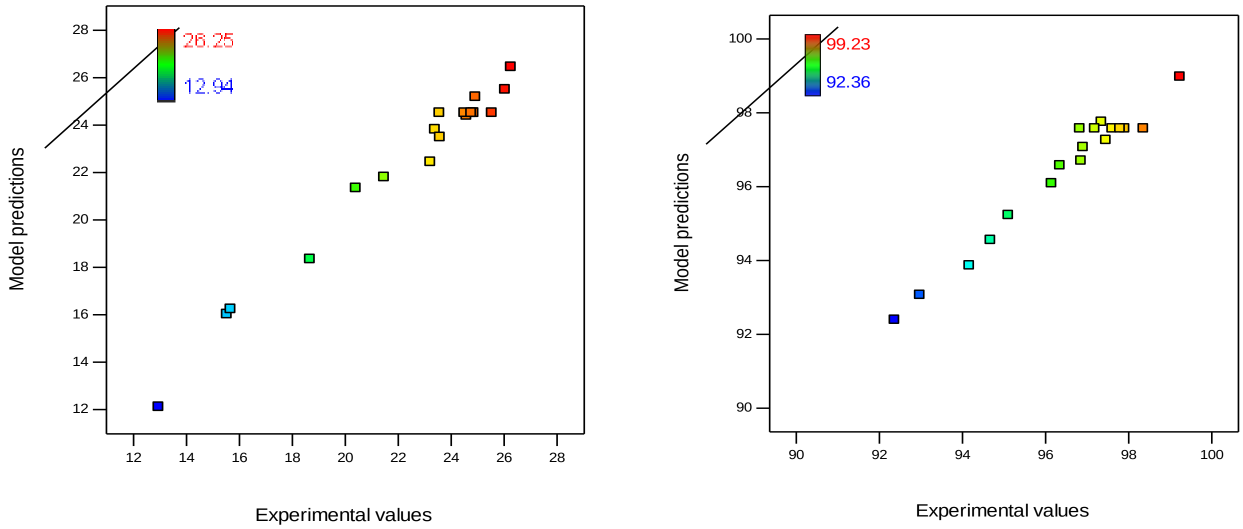


Fig. 2. Model predictions vs. actual experimental results for water flux (left) and bentazon rejection (right)

3.2. Effect of process variables on the responses

Considering RSM, the three-dimensional (3D) plots of the response surface were obtained to investigate the interactions of the process variables on the responses of water flux and bentazon rejection, as shown in Figure 3 and Figure 4, respectively.

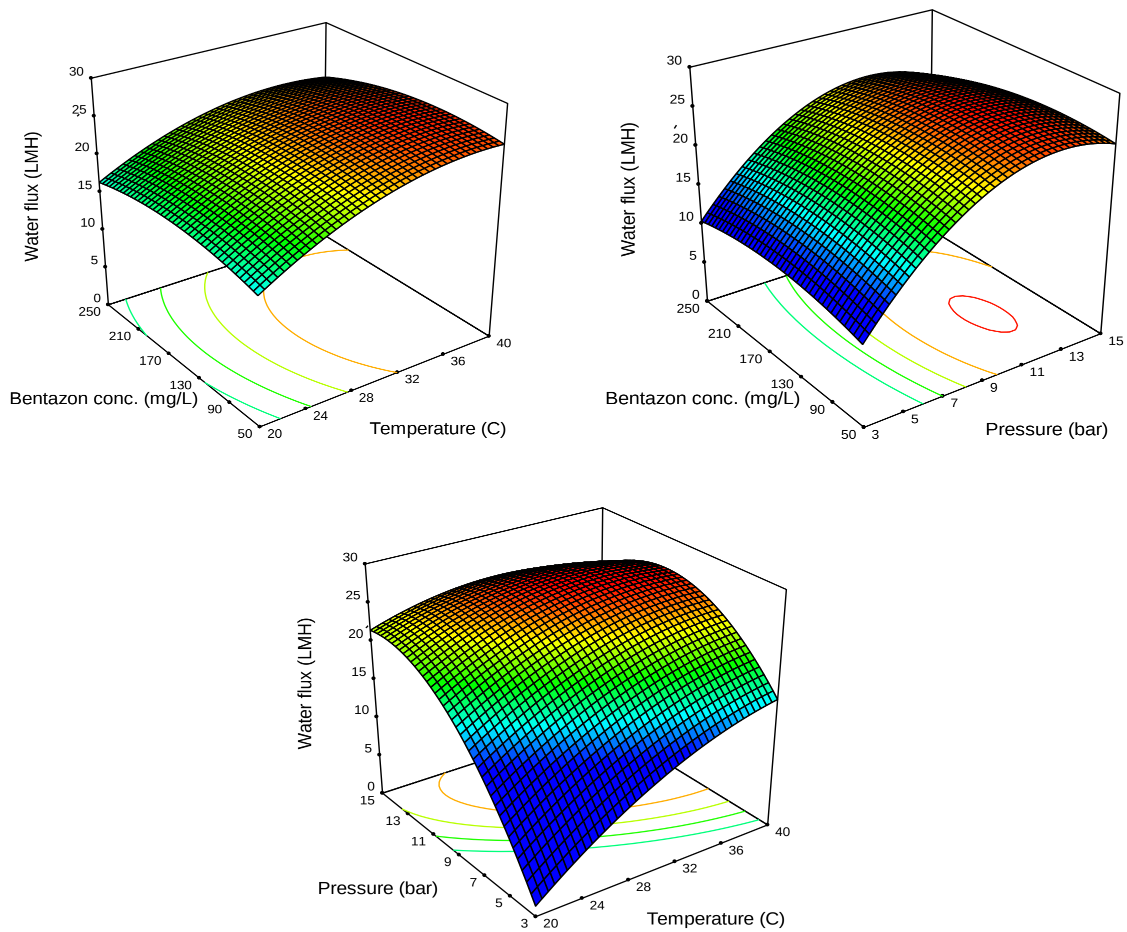


Fig. 3. Plots of 3D response surface contour for the influence of process parameters and their interactions on water flux

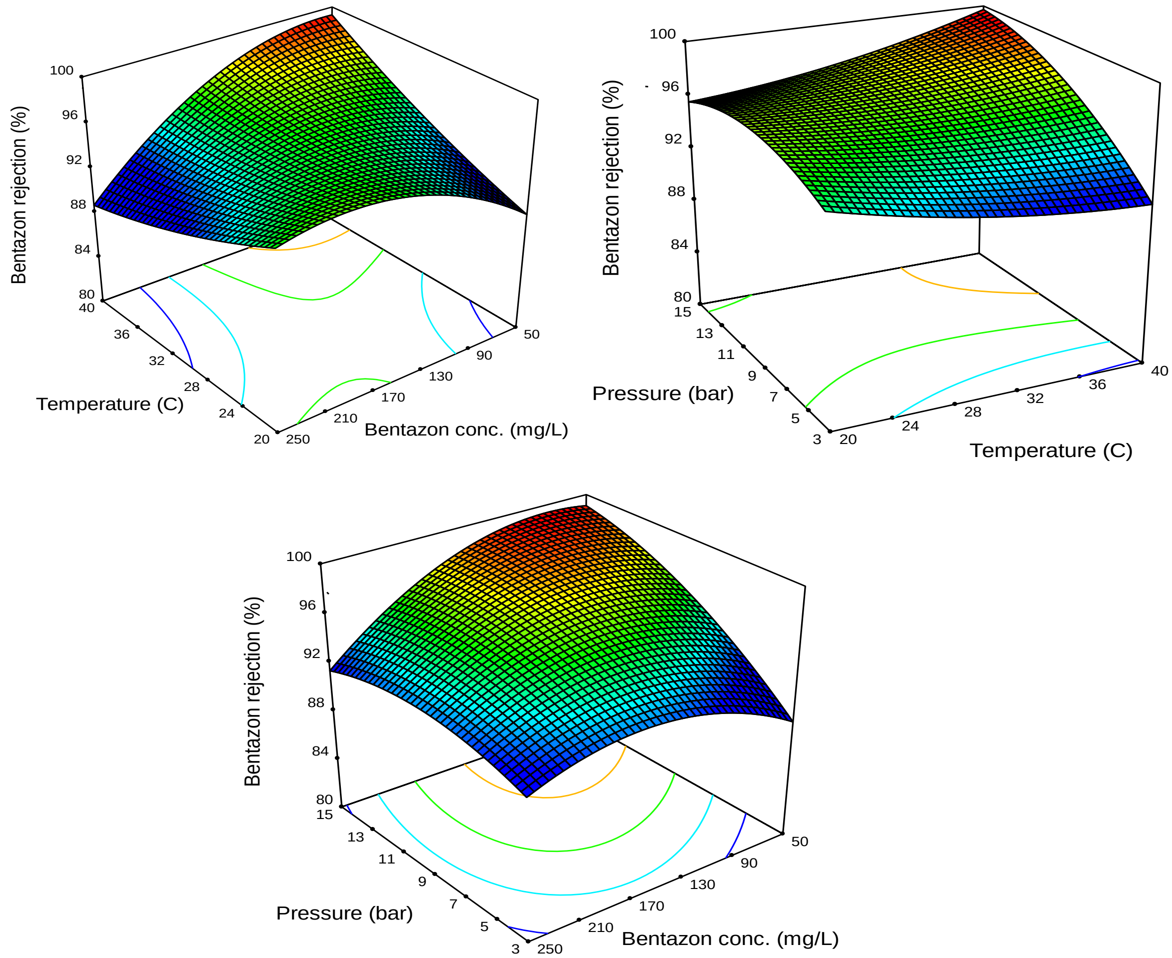


Fig. 4. Plots of 3D response surface contour for the influence of process parameters and their interactions on bentazon rejection

3.2.1. Effect of temperature

Many phenomena linked with the membrane performance depend on temperature. The temperature is one of the most important factors that considerably affect the RO membrane system in treating wastewater. To evaluate the influence of temperature on treatment efficiency, the experiments were carried out in the range of 20-40 °C. Figures 3 and 4 illustrate the 3D response surface plots of the affecting of the interaction terms on the water flux and bentazon rejection. The increasing water flux with enhancing the temperature is attributed to the lower viscosity of the water according to Darcy's law and the higher water permeability of the membrane. As the temperature increases the osmotic pressure of the feed water increases and decreases the water flux, but other influencing factors including decreasing inlet water viscosity and increased membrane permeability, both of which increase the rate of water recovery, overcome the osmotic pressure increase [27]. Bentazon concentration showed almost no effect on water flux because its concentration was very low and had no effect on the viscosity of the feed solution. The decreasing trend in bentazon rejection by a rise in temperature is a result of the higher permeability of the water molecules and pollutants through the membrane. Furthermore, the easy diffusion of water and pollutant molecules in a dense polymer at higher temperatures is a result of statistically larger fluctuations in the volumes between polymer chains because of the membrane polymer's thermal motion. For example, when compared to 20 °C, the water flux increased 1.33 and 1.40 fold at 30 °C and 40 °C, respectively, under 9 bar pressure and 150 mg/L bentazon concentration in the feed solution. It can also be observed that the decrease in the temperature and the increase in the pressure augment the bentazon rejection.

3.2.2. Influence of pressure

Hydrostatic pressure plays a very important role in pressure-derived membrane processes. The results obtained from the tests were analyzed to characterize the effects of pressure in the range of 3 to 15 bar on water flux and bentazon rejection. As seen in Figure 3, raising the pressure increased the amount of both responses. When the pressure was changed from 3 to 15 bar under 30 °C and 150 mg/L bentazon concentration in the feed solution, a

1.92 and 2.41 fold increase in the water flux and a 5.3% and 6.73% fold increase in the bentazon rejection were seen after four hours, respectively. The obtained results are in agreement with the findings of other researchers using the RO membrane for the removal of organic pollutants and pesticides [28]. In general, the solute separation increases with feed pressure to an asymptotic maximum rejection [29]; however, a decline for some organic micropollutants (e.g., estrogenic hormone) was observed when the pressure increased. This was attributed to the alteration of solute-membrane interaction by diffusion and friction, which were influenced by hydrodynamic conditions and concentration gradient [30].

3.2.3. Impact of bentazon concentration

The effect of the concentration of bentazon in the feed solution on the water flux and its removal efficiency was evaluated in the range of 50 to 250 mg/L, as shown in Figures 3 and 4. The results showed that increasing the bentazon concentration had no significant effect on the amount of water flux, which was due to the low concentration of pollutants and low osmotic pressure developed in the opposite direction to the water flux. The water flux follows Equation 5 (Fick's Law) and depends on the applied pressure and osmotic pressure difference across the membrane.

$$J=K\ (\Delta P-\Delta\pi) \qquad (5)$$

Since the concentration of bentazon is very low in the feed solution, it has a very small effect on the osmotic pressure,and its influence on the water flux is negligible. However, with increasing bentazon concentration in the feed solution, the rejection showed an increase followed by a decrease, especially at higher temperatures. This finding can be attributed to the alteration of the solute [30]. Besides, the bentazon rejection phenomenon depends on the physicochemical properties of the applied membrane and solute. The rejection of bentazon of more than 90% at different conditions in this study showed that the polyamide TFC was a high-rejection membrane in regard to bentazon by solute-membrane interactions, and therefore, the effect of the pressure on the rejection was not high. Due to the anionic nature of bentazon and negatively-charged TFC membranes, the electrostatic repulsion between them resulted in the low passage of bentazon and high rejection. The steric hindrance was also considered for this phenomenon because of the high molecular weight of bentazon [31].

3.2.4. Optimization of the bentazon rejection

Since the process factors influence the bentazon separation by the RO process, it is important to determine the optimal conditions of all the parameters to achieve maximum rejection. Table 5 represents a list of the possible optimum solutions suggested by the model for the achievement of maximum bentazon rejection along with the maximum desirability index. Based on the data of Table 5, the best removal can be achieved at a temperature of 29.8 °C, a pressure of 12.64 bar, and a bentazon concentration of 66.91 mg/L.

Table 5. Some optimal solution for maximum bentazon rejection with the best desirability index

Temperature (°C)	Pressure (bar)	Bentazon conc. (mg/L)	Bentazon Rejection (%)
28.5	14.78	119.74	99.494
27.6	14.89	60.15	99.395
29.8	12.64	66.91	100.000
28.8	13.07	101.48	99.653
29.4	13.24	114.07	99.749
32.0	10.20	70.00	99.696
27.9	13.20	81.39	99.282
27.7	13.62	94.65	99.328
27.3	14.67	80.61	99.318
27.8	14.57	99.67	99.492
27.77	14.56	101.04	99.441
28.6	12.50	106.74	99.345
29.2	13.91	106.81	99.953
38.4	7.39	113.07	99.454
33.7	10.62	130.00	99.900
29.6	11.59	113.631	99.32
29.3	13.51	119.373	99.655
39.7	7.58	121.092	99.804
27.8	14.96	100.841	99.563
33.5	9.98	130.133	99.444
27.7	14.04	105.221	99.342

4. Conclusions

In this research, RSM with CCD was employed to determine the water flux and the removal efficiency of bentazon herbicide under the low pressure of the RO process from wastewater. The results show that the TFC-RO membrane system is an effective technique for the removal of bentazon due to the solute-membrane interactions when compared to conventional methods. Three important factors of quadratic models and 3D surface response plots were evaluated by RSM using Design Expert 10 software. A second-order model equation was correlated satisfactorily by analyzing the experimental data. Based on the model, water flux increased with an increase in pressure and temperature. Furthermore, bentazon removal increased by reducing the temperature as well as increasing the pressure. With increasing bentazon concentration in the feed solution, the rejection showed an increase followed by a decrease, especially at higher temperatures. Regarding the interaction of the process factors and model equation, the water flux and bentazon rejection for different concentrations of bentazon led to different optimum points. Thus, the excellent removal of bentazon from the aqueous solution using the TFC membrane in the RO process can be considered as an effective process.

Nomenclature

Symbol

A	effective area of the RO membrane (m^2)
C	bentazon concentrations (mg/L)
J_w	water flux ($L/m^2.h$)
k	Membrane permeability
Δm	weight change of permeate (g)
R	bentazon rejection (%)
ρ	water density (g/m^3)
ΔP	applied pressure (bar)
Δπ	osmotic pressure difference (bar)
Δt	test time (h)
Index	
p	permeate side of membrane
f	feed side of membrane

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