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UF as Pretreatment of RO for Tertiary Treatment of Biologically Treated Distillery Spentwash

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Abstract**—**Distillery spentwash contains high chemical oxygen demand (COD), biological oxygen demand (BOD), color, total dissolved solids (TDS) and other contaminants even after biological treatment. The effluent can't be discharged as such in the surface water bodies or land without further treatment. Reverse osmosis (RO) treatment plants have been installed in many of the distilleries at tertiary level in many of the distilleries in India, but are not properly working due to fouling problem which is caused by the presence of high concentration of organic matter and other contaminants in biologically treated spentwash. In order to make the membrane treatment a proven and reliable technology, proper pre-treatment is mandatory. In the present study, ultra-filtration (UF) for pre-treatment of RO at tertiary stage has been performed. Operating parameters namely initial pH (pH_o: 2–10), trans-membrane pressure (TMP: 4-20 bars) and temperature (T: 15-43°C) were used for conducting experiments with UF system. Experiments were optimized at different operating parameters in terms of COD, color, TDS and TOC removal by using response surface methodology (RSM) with central composite design. The results showed that removal of COD, color and TDS was 62%, 93.5% and 75.5% respectively, with UF, at optimized conditions with increased permeate flux from 17.5 $l/m^2/h$ (RO) to 38 $l/m^2/h$ (UF-RO). The performance of the RO system was greatly improved both in term of pollutant removal as well as water recovery.

Keywords**—**Bio-digested distillery spentwash, reverse osmosis, Response surface methodology, ultra-filtration.

I. Introduction

INDIA is the Asia's second largest ethanol producer with about 2300 million liters annual production in 2006-07 [1]. Indian distilleries come under the major agro-based industry. Wastewater produced during the alcohol production is known as "spentwash". It is having high chemical oxygen demand (COD), biological oxygen demand (BOD) and dark brown color. Due to the increasing pressures from environmental regulations authorities, it is essential to treat and reuse the wastewater for achieving zero discharge. So, proper treatment is required before disposal to avoid damage to environment.

A number of technologies have been researched for treating the distillery spentwash. Biological treatment is generally considered suitable for the effluent having COD/BOD ratio 1.8-1.9 [2]. For high strength of wastewater as distillery spentwash, anaerobic treatment is acceptable and generally practiced. Biological treatment alone is not enough to meets the discharge standards and treated effluent still contains high organic matter and color. In recent years, investigations have been focused on membrane technology.

At tertiary level, reverse osmosis (RO) treatment plants have already been practiced in many bench and pilot studies in India [3], [4]. Recent work on the pilot scale using a hybrid nano-filtration (NF) and RO process demonstrated 80 to 95% rejection of the color and 55% transmission of monovalent salts at pressures of 30-50 atm [5]. Further treatment of the NF permeate using RO at an applied pressure of 50 atm removed 99% of the residual salt and produced high quality water containing negligible amounts of salt and organics that was suitable for discharge or industrial reuse. In-Soung et al. [6] demonstrated that ceramic ultra-filtration membranes could be used to reject 50% of the COD of spentwash before anaerobic digestion. This study concluded that low trans-membrane pressures (0.5 atmospheres) and high velocity (>6 m/s) are the key parameters to maintain permeability and manage the fouling.

The results with various membrane systems are promising; however, significant challenges remain in the field of membrane fouling and selecting appropriate pre-treatment system. The organic content in biologically treated spentwash is also quite high. Direct application of biologically treated spentwash to RO membrane is not advisable because of chocking and fouling of the membranes within a short span of time. To make the membrane process a reliable technology, improved process designs providing proper pre-treatment is mandatory [7], [8].

The present study evaluates the efficiency of ultra-filtration (UF) as pretreatment of RO for tertiary treatment of distillery spentwash. The purpose of this study is to optimize the UF process and evaluate the effectiveness of combined UF-RO process.

II. Materials and Methods

A. Effluent Source and Characterization

Spentwash was collected from a nearby distillery after biological treatment. The characterization of the spentwash was done as per standard method of analysis. The spentwash showed basic nature and having high COD/BOD ratio. The main spentwash characteristics were: pH= 8.0-8.3, COD= 12000-14000 mg/l, BOD= 3500-4000 mg/l, TSS= 14.5-14.8 g/l, TDS= 8.7-9.0 g/l and the color was dark brown.

B. Experimental Setup and Procedure

In this study, GE SEPA flat plate UF and RO system with thin film composite membrane was used. The membrane

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effective surface area was 0.0155 m^2. Pure water was used to determine the permeability of the membrane.

Biologically treated spentwash was used as feed for UF and treated effluent from UF was fed into RO system. The operating parameters viz. trans-membrane pressure; TMP (4-20 bars), initial pH; pH_o (2-10), temperature; T (15- 43°C) were used for UF**.** System was optimized using CCD design of response surface methodology (RSM) (discussed later). The feed was pumped into the module by using a centrifugal pump at controlled trans-membrane pressure by the pressure valve and temperature was maintained by running the hot and cold water through the jacketed tank as per the experimental run requirement.

The pH of the solution was initially measured and then adjusted as per the designed experimental runs by adding 0.1 N NaOH or 0.1 N H_2SO_4 solutions. Percentage removal of COD, color, TDS and permeate flux were assessed as responses of the UF process.

TABLE I
PROCESS VARIABLES AND THEIR LEVELS FOR UF

Variable unit	Factors	Level				
	X	-2	-1	0	1	2
Initial pH, pH_0	X_1	2	4	6	8	10
Temperature (°C)	X_2	15	22	29	36	46
Trans-membrane Pressure (bar)	X_3	4	8	12	16	20

Contaminants removal (COD color and TDS) before and after each experimental run were measured. COD was measured using digestion unit (DRB 200, HACH, USA) and UV visible spectrophotometer (HACH, DR 5000, USA). TDS and color were measured by double beam UV-visible spectrophotometer (HACH, DR 890, USA).

Percentage removal of these contaminants was calculated by using following relationship, Percentage removal:

$$(Y) = 100(Z_o - Z_t)/Z_o \quad (1)$$

where, Z_o is initial concentration of contaminants (COD, color and TDS) and Z_t is the the concentration of contaminants after specified time (COD, color, and TDS).

$$J = V/A * t \quad (2)$$

where, J is permeate flux, V is permeate volume, A is effective membrane area and t is the time.

Permeate flux (J) is the amount of sample collected per unit area per unit time. It was calculated by dividing the permeate volume (V) divided by the product of effective membrane area (A) and time (t) [9].

C. Experimental Design

Optimization of the operating parameters for UF membrane was done using CCD design of response surface methodology on the basis of few sets of experiments.

Three factors with five levels have been used for the experimental design of UF system. For statistical calculations, the levels were coded as X_i according to the following relationship [10]:

$$X_i = (X_i - X_o)/\delta X \quad (3)$$

where, X_o is value of the X_i at the center point and δX represents the step change. The different variables and their levels for SS electrodes and RO system are given in Table I.

III. RESULTS AND DISCUSSIONS

A. Optimization of UF

Performance of a membrane process is generally affected by trans-membrane pressure, temperature and pH of the system. Optimization of the operating parameter plays an important role in the effectiveness of a process. UF membrane system was optimized with three operating parameter initial pH; pH_o (2-10), temperature; T (15-43°C) and trans-membrane pressure; TMP (4-20 bars). Central composite design was used to study the effect of different operating parameters on permeates flux and contaminant removal (COD, color, and TDS) by conducting different combination of experiments. Actual and predicted values of permeate flux and percentage removal of COD, color and TDS by UF process is shown in Table II. To obtain the regression equations from the linear, interactive, quadratic and cubic model, quadratic model was found to be best fitted with the experimental data.

Final Equation in Terms of Coded Factors:

$$COD = +47.74 - 0.51 \times A - 4.50 \times B + 5.08 \times C - 4.75 \times A2 + 1.32 \times B2 + 2.55 \times C2 + 3.04 \times A \times B + 3.85 \times A \times C - 6.27 \times B \times C \quad (4)$$

$$Color = +96.07 - 0.58 \times A - 0.098 \times B + 0.41 \times C - 0.058 \times A2 + 8.687E - 003 \times B2 + 0.11 \times C2 + 9.055E - 003 \times A \times B - 0.22 \times A \times C - 0.076 \times B \times C \quad (5)$$

$$TDS = +28.15 - 0.22 \times A - 0.46 \times B + 4.03 \times C + 1.82 \times A2 + 0.82 \times B2 + 0.73 \times C2 - 1.18 \times A \times B + 0.53 \times A \times C - 1.22 \times B \times C \quad (6)$$

$$\text{Permeate flux} = +30.52 + 1.26 \times A + 2.91 \times B + 8.95 \times C - 2.71 \times A2 - 0.55 \times B2 - 0.87 \times C2 - 0.48 \times A \times B - 0.29 \times A \times C + 1.35 \times B \times C \quad (7)$$

Regression coefficient and p value for different responses with UF optimization is given in Table III. The value of F from the analysis of variance (ANOVA) for COD, color, TDS removal and permeate flux is 6.7, 6.4, 10.7, and 46.25, respectively.

The p value less than 0.05 signify that the model is statistically significant [11] and the terms of coefficient are more significant, if the value of 'F' is larger than value of 'p' [12]. The p value of model for COD, color, TDS removal and permeate flux are significantly low (0.003, 0.0039, 0.0005 and 0.0001, respectively), indicating that model fits close to the experimental results [13].

TABLE II
EXPERIMENTAL DATA AND FITS FOR UF EXPERIMENTS

Run	pH	Temp. (°C)	Pressure (bar)	%COD removal		%Color removal		%TDS removal		Permeate flux	
				actual	predicted	actual	predicted	actual	predicted	actual	Predicted
1	6	20	12	42.07	47.42	94.61	94.71	24.27	26.31	13.55	13.85
2	6	25	12	34.03	32.63	96.50	96.33	28.33	27.18	16.65	17.91
3	6	33	12	39.11	44.87	95.02	94.68	31.77	30.20	18.58	17.93
4	6	25	12	41.56	42.23	96.01	96.26	24.20	26.34	18.97	20.05
5	4	20	8	58.48	62.40	96.40	96.12	38.21	35.75	29.03	29.62
6	4	20	16	64.18	63.01	96.57	96.88	37.46	38.72	30.19	32.52
7	8	30	16	28.80	34.79	95.65	95.79	33.92	34.75	38.71	39.12
8	6	25	12	48.31	47.55	96.64	96.51	35.36	33.00	38.71	40.09
9	6	25	20	37.98	29.77	94.50	94.67	35.47	35.88	16.65	17.16
10	8	30	8	24.13	27.75	97.15	97.01	35.09	34.99	24.39	22.20
11	6	25	12	57.30	53.56	96.16	96.18	29.38	29.44	30.97	27.05
12	4	30	16	49.07	43.89	95.90	95.93	29.28	29.71	34.84	33.85
13	6	25	12	50.70	47.80	94.73	94.79	23.92	23.04	9.29	9.13
14	2	25	12	69.79	68.10	96.48	96.45	37.94	39.14	46.45	44.94
15	8	20	16	43.44	47.74	95.83	96.07	27.11	28.15	30.97	30.52
16	4	30	8	41.81	47.74	95.83	96.07	26.08	28.15	30.97	30.52
17	6	25	4	49.24	47.74	96.16	96.07	28.25	28.15	30.97	30.52
18	6	25	12	48.82	47.74	95.51	96.07	27.94	28.15	29.03	30.52
19	8	20	8	52.50	47.74	96.88	96.07	30.10	28.15	30.19	30.52
20	10	25	12	50.91	47.74	96.22	96.07	29.28	28.15	29.42	30.52

The R-square values for COD, color, TDS removal and permeate flux are 0.8575, 0.8511, 0.9056 and 0.9765, respectively given in Table III. Results of ANOVA for UF system show that the selected model explains the factor response interaction correctly. The value of permeate flux and removal efficiency for COD, color and TDS is found close to optimum values. The actual and predicted values of responses given in Table II shows that the residuals for the prediction of each response are minimum. It indicates that the results of ANOVA analysis are correct [10], [11].

B. Effect of Various Operating Parameters

The three-dimensional response surface graphs for all responses with different variables are shown in Figs. 1 and 2. Trans-membrane pressure, temperature and pH of the system affect the membrane performance. Removal efficiency of COD, Color and TDS increases as the pH approaches to the neutral. Reason could be that at highly acidic and basic condition, pollutants are in their maximum dissolved form which results in their easy passage through membrane. At the optimum T, around 25 °C, removal efficiency is maximum. Further increase in T results in decreased removal efficiency of the pollutants. This could be due to increased solubility and diffusion of the solute with increase in T. Permeate flux increases as the pH and T increases due to increase in the permeability of water [14].

With the increase of the TMP, removal efficiency of COD, color and TDS is also increased. As the UF membrane has lower pore size compared to MF, at higher pressure formation of concentration polarization at membrane surface could result in higher pollutant removal. Permeate flux also increases as the TMP increases due to increase in permeability of water through the membrane.

C. Optimized Conditions

To maximize the COD, color and TOC removal efficiencies with maximum permeate flux, multi-objective optimization of operating parameters of UF system was done using desirability function approach. The optimum value of operating parameters after examining the response curves were: pH=6.9; T=20°C; and TMP=46.2 bar for RO and pH=6.9; T=20°C; and TMP=16 bar for UF respectively. The maximum predicted COD, color, TDS removal was 62%, 93.5% and 75.5%, respectively with permeate flux 33 $l/m^2/h$. At optimum conditions, three ratification experiments were carried out and the actual values obtained by ratification experiments were within 95% confidence interval of the predicted value.

TABLE III
ANALYSIS OF VARIANCE FOR %COD, COLOR, TDS REMOVAL AND PERMEATE FLUX BY UF

	COD				Color				TDS				Permeate Flux			
Source	Sum of Square	DF	F Value	P value	Sum of Square	DF	F Value	P value	Sum of Square	DF	F Value	P Value	Sum of Square	DF	F Value	P Value
Model	2043.05	9	6.68	0.0032	9.08	9	6.35	0.0039	379.30	9	10.66	0.0005	1620.17	9	46.25	<0.0001
Residual	339.62	10			1.59	10			39.53	10			38.93	10		
Lack of fit	249.92	5	2.79	0.1426	0.48	5	0.43	0.8093	29.04	5	2.77	0.1440	35.20	5	9.46	0.0138
Pure error	89.70	5			1.11	5			10.49	5			3.72	5		
Total	2382.67	19			10.67	19			418.82	19			1659.09	19		
R-square	0.8575				0.8511				0.9056				0.9765			

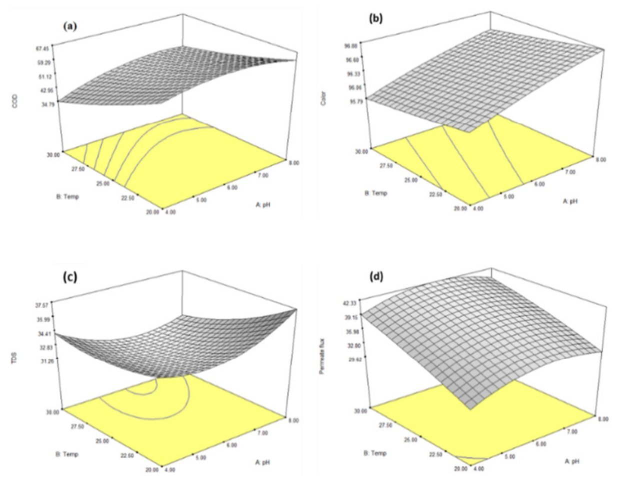

Fig. 1 Effect of pH and T, on (a) %COD removal (b) %color removal (c) %TOC removal and (d) permeate flux

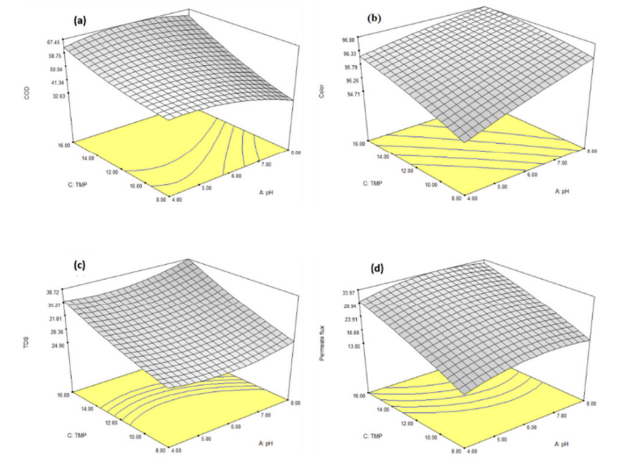

Fig. 2 Effect of pH and TMP on (a) %COD removal (b) %color removal (c) %TOC removal and (d) permeate flux

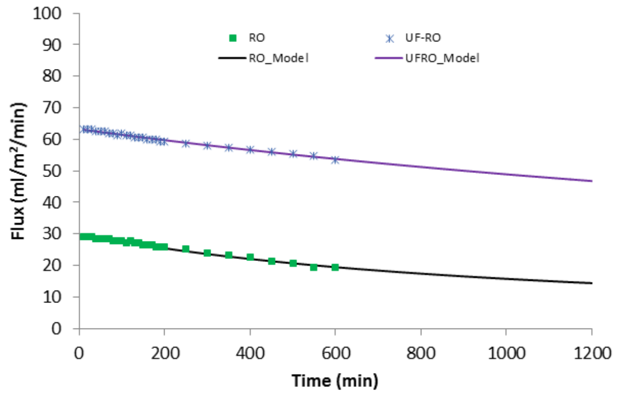

Fig. 3 Flux decline profile of RO system and combined with UF pre-treatment

D. UF-RO Combined Treatment at Optimized Conditions

The performance of the UF followed by RO system at optimized conditions coming out from the CCD design of RSM, in terms of removal percentage of different contaminants (COD, color, TDS and TOC etc.) was 99%, 99.2% and 98.5%, respectively, with increased permeate flux from 17.5 $l/m^2/h$ to 38 $l/m^2/h$ after using UF pre-treatment. Effect of filtration time on permeate flux of RO was studied at optimized condition. Flux versus time curves of RO were analyzed using modified form of Hernia's model [9] to evaluate the effect of pretreatment on flux decline mechanism. Permeate flux profile of RO with and without UF pre-treatment is shown in Fig. 3. Results showed that the initial flux of UF-RO is almost double of flux with RO alone. The decrease in flux was more with RO as compared to the flux with UF-RO, which is more or less steady. This study was conducted for 3 hrs to show the effect of pre-treatment on permeate flux. Reduction in flux indicated that the fouling potential of the spentwash with time. Permeate flux is a measure of membrane performance and it decreases due to fouling of the membranes [15]. The best fitted model for RO membrane fouling follows the intermediate blocking filtration, assuming that all the particles doesn't block the membrane pores. They may settle on other particle [9]. Intermediate blocking filtration model equation is given as:

$$1/Q = K_t t + 1/Q_o \qquad (8)$$

where, Q is permeate flow rate, Q_o is initial permeate volume, t is time and K_t is the filtration constant.

The permeate flux data was fitted in to the intermediate blocking filtration model equation. The graph was extrapolated to find out the filtration pattern of RO alone and with UF pre-treatment. The study revealed that permeate flux of RO increased by almost 2 times with UF pre-treatment which also increased the life of the RO membrane system as compared to RO system alone. It also improves the quality of the effluent which can be reused with in the industry. In terms of the cost of the treatment setup, although adding pretreatment facility adds extra cost but the overall payback period is reduced due to increase in water production.

IV. Conclusion

Present study concluded that the UF system seems to be effective pre-treatment option of RO as tertiary treatment for the biologically treated distillery spentwash. UF process improved the treatment efficiency of the RO process as well as life of RO membrane system. Amount of water recovered from UF-RO process was almost double to that of the amount recovered from RO system alone. Permeate flux of RO process was increased from 17.5 to 38 l/m2/h with UF pretreatment. Maintenance, cleaning and frequency of membrane replacement could also be reduced and a reusable quality of permeate was recovered as resource, which can be used within the process itself and helps in meeting the zero discharge standards.

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