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PDMS/ceramic composite membrane synthesis and evaluation of ciprofloxacin removal efficiency

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Abstract−The present study employs an unexplored, one-step route for remediation of ciprofloxacin, an emerging contaminant, using hydrophobically modified ceramic membranes. Hydrophobic interaction between the membrane and the target contaminant, i.e., ciprofloxacin, is the governing factor responsible for its removal. The hydrophilic surface of hollow, single channel, macroporous clay-alumina membranes was made hydrophobic using cross-linked polydimethylsiloxane. The influencing parameters--concentration of polymer, cross-linking agent, catalyst and coating time--were optimized by Taguchi analysis to yield a membrane with enhanced ciprofloxacin rejection and high permeate flux. The synthesized membrane was characterized for its contact angle, clean water permeability, degree of swelling, degree of cross-linking, X-Ray diffraction, atomic fluorescence microscopy, field emission scanning electron microscopy. Effect of various operating parameters--cross flow velocity, transmembrane pressure, filtration time, solution pH--was investigated upon removal of ciprofloxacin in cross flow membrane filtration. Maximum rejection of 99.3% was obtained by the hydrophobic membrane having contact angle of 138.5° for 5 mg/L feed solution. The stability of the membrane was judged in terms of change in ciprofloxacin rejection upon filtration for five consecutive cycles, each cycle being 180 min. The developed PDMS/ceramic composite membranes could have great prospect for long-term application in removal of emerging contaminants from water.

Keywords: Ciprofloxacin, Polydimethylsiloxane, Hydrophobic, Taguchi, Ceramic Membranes

INTRODUCTION

Antibiotics, a class of pharmaceuticals, are presently being considered as toxic emerging contaminant and are broadly classified under the group of Pharmaceutical and Personal Care Products (PPCP) [1]. Rising urbanization and growing population have led to an increased use of antibiotics. This leads to their amplification in wastewater, which may inhibit microorganisms mediated processes like carbon-nitrogen cycles and nutrient regeneration [2,3]. Hence, their removal from aqueous system is necessary. Ciprofloxacin, our target contaminant is a widely used second generation fluroquinolone group of antibiotics, active against different types of bacteria [4]. Incomplete metabolism of a pharmaceutical in the human body, lack of proper strategy for wastewater treatment in the pharmaceutical industries and common wastewater treatment plants (WWTP) have led to abundance of ciprofloxacin in aqueous systems in a wide concentration range of ng/L to mg/L [5-7]. It has also been listed among top ten pharmaceuticals of high priority according to a European assessment committee [8]. Its high solubility and stability in aqueous solution at different pH and difficulty in biodegradation is also responsible for their increased concentration in wastewater. Data from certain hospital wastewater shows about 124.5 μg/L ciprofloxacin, whereas about 313-568 ng/L concentration was detected in effluent of WWTP [9]. The concentration of the antibiotic was found to be as high as 6.5 mg/L in river water [10] and about 50 mg/L in pharmaceutical plant wastewater [7]. In India, about 31 mg/L ciprofloxacin was detected in the effluent of WWTP [11]. Ciprofloxacin contaminated wastewater was found to adversely affect human health and aquatic flora and fauna. It may restrain the photosynthesis process in plants, thus causing a severe ecological imbalance [12]. Hence, remediation of ciprofloxacin from discharge streams has become a topic of major concern.

Various potential approaches have been employed for remediation of ciprofloxacin from water. This includes conventional methods like adsorption, biodegradation, activated sludge process, ozonation [7,13-15], as well as advanced separation techniques: photocatalytic degradation [9,16,17] and membrane separation [12,18]. High adsorption capacity of 235.6 mg/g was attained for ciprofloxacin removal using 3D porous graphene hydrogels [4]. However, the fate of the spent adsorbent is still an unexplored area. Reduced grapheme oxide-TiO_2 nanotube (RGO-TON) hydrogel was reported to be highly efficient in removal of the target contaminant due to amalgamation of the adsorptive property of graphene and photocatalytic property of TiO_2 [19]. However, advanced oxidation processes may result in toxic by-product formation [16]. About 80% sorption of ciprofloxacin on activated sludge surface was attained because of its high sorption constant [20]. Membrane separation of these low molecular weight compounds is based on multiple mechanisms: size exclusion, adsorption, hydrophobic interaction, elec-

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trostatic interaction, steric effect [21]. A high flux, fouling resistant hollow fiber nanofiltration (NF) membrane prepared by hyperbranched polyethyleneimine was successful in removal of about 99% ciprofloxacin, the removal being strongly pH dependent [12]. The performance efficiency of nine polymeric NF membranes for ciprofloxacin removal was analyzed and solution pH, pore size were found to be the dominant factors responsible for separation [22]. However, use of high pressure NF and reverse osmosis membranes makes the process costly. Moreover, polymeric membranes limit their large scale application because of lower thermal, mechanical, chemical stability and longevity compared to ceramic membranes [23]. The current study thus aims at application of indigenously developed ceramic membranes for ciprofloxacin separation from water upon hydrophobic surface modification by polydimethylsiloxane (PDMS). PDMS membranes are widely applied for pervaporation involving separation of a mixture of liquids based on selective diffusion/permeation into the membrane surface [24]; however, studies on such PDMS/ceramic membrane process for separation of ciprofloxacin via hydrophobic interaction have not been reported till date.

Permutation and combination of different control parameters for hydrophobic membrane formation was performed with the aid of Taguchi analysis. The optimized membrane should result in maximum ciprofloxacin rejection along with maintenance of high permeate flux. ANOVA analysis was done to study the interaction among the independent factors: amount of chemicals added and coating time. Thus the process emerges to be highly effective in removal of toxic organic contaminants from water.

EXPERIMENTAL

1. Materials

Ceramic macroporous support tubes were prepared from optimized composition of clay-alumina mixture by extrusion [23]. The tubes were hollow, single channeled having external diameter: internal diameter of 10 mm: 7 mm, the average pore size being 1 μm and porosity 39%. The target emerging contaminant ciprofloxacin was purchased from Sigma Aldrich, Germany. Hydrophobic modification of the support tubes was made using the hydrophobic polymer polydimethylsiloxane (PDMS, Sigma Aldrich, USA) having viscosity of 1,800-2,200 cSt, tetraethyl orthosilicate (TEOS, Sigma Aldrich, USA) and dibutyltin dilaurate (DBTDL, Sigma Aldrich, USA) which were used as cross linker and catalyst, respectively.

2. Preparation of Hydrophobic Membranes

2-1. Experimental Design for Membrane Preparation

Effect of independent parameters (amount of PDMS, TEOS, DBTDL taken and coating time) were analyzed on clean water permeability, ciprofloxacin rejection and contact angle of the membrane. Reports show that highly viscous, concentrated PDMS coating slurry results in increased active layer thickness, which is detrimental to permeate flux, whereas less viscous PDMS solution results in penetration within the pores of the support tube, resulting in a defective, inhomogeneous coating [25]. Thus, the coating parameters should be optimized to attain slurry of specific viscosity, which would lead to uniform highly hydrophobic coating on the surface, along with high flux and rejection of the pharmaceutical component. The present study employs fractional factorial design, i.e., Taguchi orthogonal array (OA) design for efficient conduction of minimum number of experiments followed by subsequent statistical analysis and optimization [26]. It was done using Design Expert 6.0.8. software. Random choice of process parameters may result in defective, inhomogeneous coating. Hence, optimization is an important process to attain good membrane performance. Previously, univariate approach of one-factor-at-a-time was used which used to consume more time, chemicals and also lack of proper understanding of the interaction effects. Thus, to meet the disadvantages, multivariate is used ,which gives statistical information for the entire experimental range unlike the univariate approach [27]. The main influencing parameters and two factor interactions are considered in Taguchi design, with the assumption of non-existence of higher order interactions. Based on the number and levels of process parameters, suitable OA is selected for analyzing their simultaneous interactions on the response. In the current study, interactive effects of four factors were considered: the amount of coating materials taken and coating time, each factor being judged at three levels, i.e., L9 OA. A systematic, unique, simple, user friendly, time-saving approach for statistical analysis is provided by Taguchi OA design approach compared to artificial neural network (ANN) and response surface methodology (RSM) [27-29].

Table 1 represents the range of independent parameters selected: concentration of PDMS (A), crosslinking agent TEOS (B), catalyst DBTDL (C) and coating time (D). The high (+1) and low levels were chosen based on the prior preliminary experimentation. The responses were contact angle (°) (which determines membrane hydrophobicity), clean water permeability ($Lm^{-2}h^{-1}bar^{-1}$) and ciprofloxacin rejection (%). Table 2 represents the experimental design performed to analyze the effects of various coating parameters upon the responses.

ANOVA was used to study the significant percentage contribu-

Table 1. Range and level of independent parameters

Independent variable	Range and level		
	1	2	3
PDMS (ml) (A)	2.5	5	7.5
TEOS (ml) (B)	0.5	1	1.5
DBTDL (ml) (C)	0.02	0.04	0.06
Coating time (min) (D)	2.5	5	7.5

Table 2. Taguchi experimental design

Experiment	A	B	C	D
1	5	0.5	0.04	7.5
2	7.5	1	0.02	7.5
3	2.5	1	0.04	5
4	5	1	0.06	2.5
5	7.5	1.5	0.04	2.5
6	2.5	0.5	0.02	2.5
7	5	1.5	0.02	5
8	7.5	0.5	0.06	5
9	2.5	1.5	0.06	7.5

tion of different independent controlling parameters by estimating the associated variance ratio (F-value) and the error. The relation between sum of squares (SS), mean of square (MS), degrees of freedom (DOF), F-value (5% significance level) can be calculated according to established equations [30]. In Taguchi analysis, for each independent factor, the fraction of the total variance leads to their significant percentage contribution (P (%)) to the response.

2-2. Preparation and Characterization of Hydrophobic Membranes

The map of experiments as set by Taguchi OA design is represented in Table 2. The support tubes, 150 mm long, were ultrasonicated with acetone and oven dried to remove any impurities. These tubes were then coated with PDMS as the hydrophobic agent. The coating slurry was prepared by dissolving PDMS in *n*-hexane (25 ml), followed by TEOS and DBTDL addition in different ratio at room temperature as shown in Table 1, and mixed properly to attain homogeneous solution. The coating protocol was similar to that of other researchers [31] with some modification in the coating parameters. Care had to be taken for complete dissolution of PDMS, else it would lead to inhomogeneous coating of the tubes. The entire process was performed in inert atmosphere by purging nitrogen to avoid presence of humidity. Dip coating method was used for coating the external and internal surface of the tubes with the prepared slurry at different coating time varying from 2.5 min to 7.5 min as shown in Table 1. Unsupported PDMS films were prepared by evenly spreading the coating slurry in a petri plate. The coated tubes and PDMS films for all the nine sets of experiments (Table 1) were cured at 80 °C for 12 h in air oven for complete removal of the solvent and to attain proper crosslinking.

The microstructural observation of the macroporous support tubes and optimized hydrophobic membrane, pre and post ciprofloxacin filtration was done using field emission scanning electron microscopy [FESEM, Zeiss, Germany]. atomic force microscopy (AFM, Nanonics, Israel) was used to analyze the surface roughness and topology of the prepared composite membrane. Contact angle was measured using a goniometer (Kruss, Germany) using sessile drop method to assess surface hydrophobicity of all the tubes. About 2 μL water was used as wetting medium at 25 °C and the average of three measurements taken at different locations on the membrane surface, having mean error of ±1° was reported. The clean water permeability of the composite membranes was calculated by measuring permeate flux of milliQ water at different transmembrane pressure from 0.5 bar to 5 bar. The membranes were soaked in water for 24 h, before conducting the experiment, and about 10 min time was provided before collection of permeate at a particular pressure to attain a stable flux. X-ray diffraction (Phillips 1710 Diffractometer, Netherlands) was used for analysis of composition of PDMS membrane (unsupported film) in the scanning range of 5° to 80°. Fourier transform infrared spectroscopy (FTIR, PerkinElmer, USA) of the PDMS membrane, pre- and post ciprofloxacin removal was performed for identification of the various functional groups in the wave number range of 400-4,000 cm^{-1} and identify the mechanism of ciprofloxacin removal by the membrane. The stability of the membrane in acidic and basic medium was judged by dipping the membrane in aqueous solution of pH ranging from 1 to 14 and measuring the change in weight. The swelling of the PDMS membrane in target medium water was assessed by measuring the gain in weight of the wet, swollen membrane (M_s) upon immersing in water for 24 h [31]. The degree of cross linking (DC) of the membrane was estimated by finding the change in weight upon immersing in the organic solvent hexane (M_h).

3. Removal of Ciprofloxacin by the Hydrophobic Membranes

The effectiveness of the all prepared membranes was analyzed for ciprofloxacin removal. Deionized water was spiked with 0.5 mg/L to 5 mg/L of ciprofloxacin, in accordance with the concentration found in wastewater and surface water. The laboratory scale water filtration setup was comprised of a feed tank made of stainless steel and 10 L capacity, connected to a perplex membrane module. The flow velocity of feed solution from tank to membrane module was controlled by a recirculating piston pump, providing maximum pressure of 6 $kgcm^{-2}$ and a flowmeter having maximum flowrate of 20 LPM. The connectors were stainless steel to enable rust-free conditions and suitable for sustaining high pressure. Valves and pressure gauges present at inlet and outlet of membrane module regulated the flow and pressure, respectively. A clean, contaminant-free permeate was collected from the module outlet, whereas the concentrated retentate was returned to the feed tank.

The optimized hydrophobic membrane prepared on the basis of maximising the contact angle, permeate flux, ciprofloxacin rejection was selected for further study. Effect of different operating conditions (transmembrane pressure (TMP), cross flow velocity (CFV), filtration time on permeate flux and ciprofloxacin rejection) was studied. Effect of solute properties like initial concentration, pH of feed solution was also found to affect the filtration performance of the contaminants. Solubility of ciprofloxacin is highly pH dependent, the value ranging from 6.19 g/L to 0.15 g/L on increasing pH from 5 to 7. When the solution pH is below the pK_{a1} value of 5.9, cationic from of ciprofloxacin is predominant due to protonation of amine group, whereas on increasing pH above its pK_{a2} value of 8.89, the anionic form exists due to deprotonation of carboxylic group. At pH between 5.9 to 8.89, it exists as an uncharged, zwitterionic species [32]. Thus, a membrane separation study of the target antibiotic was carried out at three different pH (4.5, 6.8, 9.5) at which ciprofloxacin was present in all three ionic states. The rejection of a component by membrane filtration was measured according to Eq. (1). Ciprofloxacin concentration was determined using UV-Visible spectrophotometer at λ_{max} of 280 nm [33]. Upon scanning the absorbance of ciprofloxacin solution in the UV range (200-400 nm), maximum wavelength (λ_{max}) was found to be at 280 nm [33]. Thus, concentrations of the different solutions were obtained from the absorbance versus standard (known) concentration calibration curve.

$$\text{Rejection} = 1 - C_p/C_f \quad (1)$$

where, C_f, C_p is the concentration of the contaminant in feed solution and permeate, respectively. The process efficiency for long-term applications was analyzed by continuous filtration of ciprofloxacin for five repetitive cycles, each cycle being performed for 3 h at a stretch. The membrane fouling was minimized by providing pneumatic backpulsing at optimized conditions of backwash pressure, duration and relaxation interval to minimize fouling. The membrane was thoroughly washed with distilled water after completion of each experiment and its antifouling property was esti-

Table 3. Experimental and model predicted values of the responses

Runs	Experimental			Predicted		
	Contact angle (°)	Clean water permeability ($Lm^{-2}h^{-1}bar^{-1}$)	Ciprofloxacin rejection (%)	Contact angle (°)	Clean water permeability ($Lm^{-2}h^{-1}bar^{-1}$)	Ciprofloxacin rejection (%)
1	141.2	106.8	97.6	142.31	112.93	98.29
2	146.2	100.6	98.9	146.31	102.80	101.06
3	131.2	160	85.7	128.41	159.80	87.06
4	125.8	192	84.7	125.24	184.80	86.02
5	132.7	176	91.6	129.24	174.67	88.79
6	114.5	200	78.8	118.51	208.53	80.29
7	135.7	135	94.8	135.14	136.07	92.79
8	135.8	126.8	94.9	139.14	125.93	95.56
9	136.8	145	95.4	135.58	136.67	92.56

mated by calculating the flux recovery ratio (*FFR*) [34]. The mechanism of removal of target components by hydrophobic membranes was also investigated by FTIR analysis of the PDMS film, at nascent and post filtration conditions. The sustainability of the membrane in water filtration application was judged by the change in contact angle upon its exposure to target contaminant for 30 days.

RESULTS AND DISCUSSION

1. Statistical Analysis for Hydrophobic Membrane Preparation

The macroporous support tubes were coated with the slurry as obtained from experimental design by Taguchi method. The experimental and model predicted values of the responses obtained under experimental conditions (Table 2) are represented in Table 3. Fig. 1 shows the contact angle of the hydrophobic membranes prepared according to Table 2 varies from 114° to 146°.

Maximum ciprofloxacin rejection of 98.9% was obtained by the membrane having contact angle 146.3° but low permeation of 100.6 $Lm^{-2}h^{-1}bar^{-1}$. The plot of model predicted versus experimentally obtained data of the three aforementioned responses is shown in Fig. 2(a)-(c). The goodness of fit of the model is explained in terms of coefficient of determination (R^2). The R^2 was found to be 0.93, 0.97, 0.93 for contact angle, clean water permeability, ciprofloxacin rejection, respectively. Moreover, the difference between the predicted R^2 and adjusted R^2 values was less than 0.2 for all the responses, indicating good match between them [35].

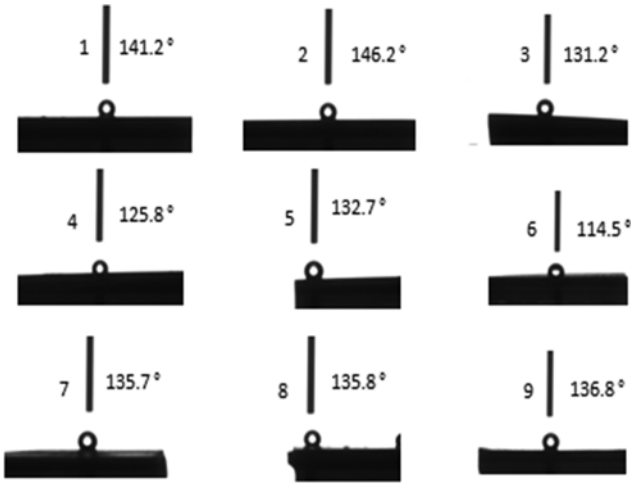

Fig. 1. Contact angle of the PDMS membranes prepared according to different experimental conditions.

The effect of independent parameters upon the dependent responses was studied by analysis of variance (ANOVA). It incorporates the underlying principle of total corrected sum of squares (SST), error sum of squares (SSE), regression sum of squares (SSR) having n−1, n−k−1, k degrees of freedom respectively [24]. F-test guides the acceptance or rejection of hypothesis at α level of significance [27]. Based on the probability (p) whether the calculated F-value exceeds a theoretical value, the model having the highest order and statistically significant terms was selected. Higher F value resulting in low probability (p value usually less than 0.05) justifies reliability of the relation between the variables.

The ANOVA for the responses was performed to study the effects of PDMS, DBTDL, TEOS addition and dip coating time (Table 4). The probability (p value) is less than 0.05, indicating significant effect of the amount of PDMS added and dip coating time, whereas DBTDL, TEOS have negligible effect for all the responses. Higher F-value indicates greater effect of the independent parameter. The same observation can be concluded from the relative percentage contribution of the parameters as shown in Fig. 2(d). It shows maximum contribution of coating time for all the responses especially for clean water permeability. The effect of variation of the catalyst TEOS dosage was found to be the least effective among all the experimental parameters. The errors in the experiment produced due to uncontrollable noise can be found from Table 4. The calculated error for the contribution of factors was 0.18%, 0.02%, 0.2% for contact angle, clean water permeability, ciprofloxacin rejection, respectively. These show the errors fall within the considerable limit of 50%, making the results reliable and the errors insignificant [30].

Thus, it can be concluded that the membrane properties and efficiency depend upon their preparation conditions. Increase in polymer concentration and coating time leads to increase in active layer thickness [24]. This results in reduced permeability and increased transport resistance. When the polymer concentration increased from 2.5 ml to 7.5 ml, at constant coating time of 5 min, the permeability was reduced from 160 $Lm^{-2}h^{-1}bar^{-1}$ to 126.8 Lm^{-2}

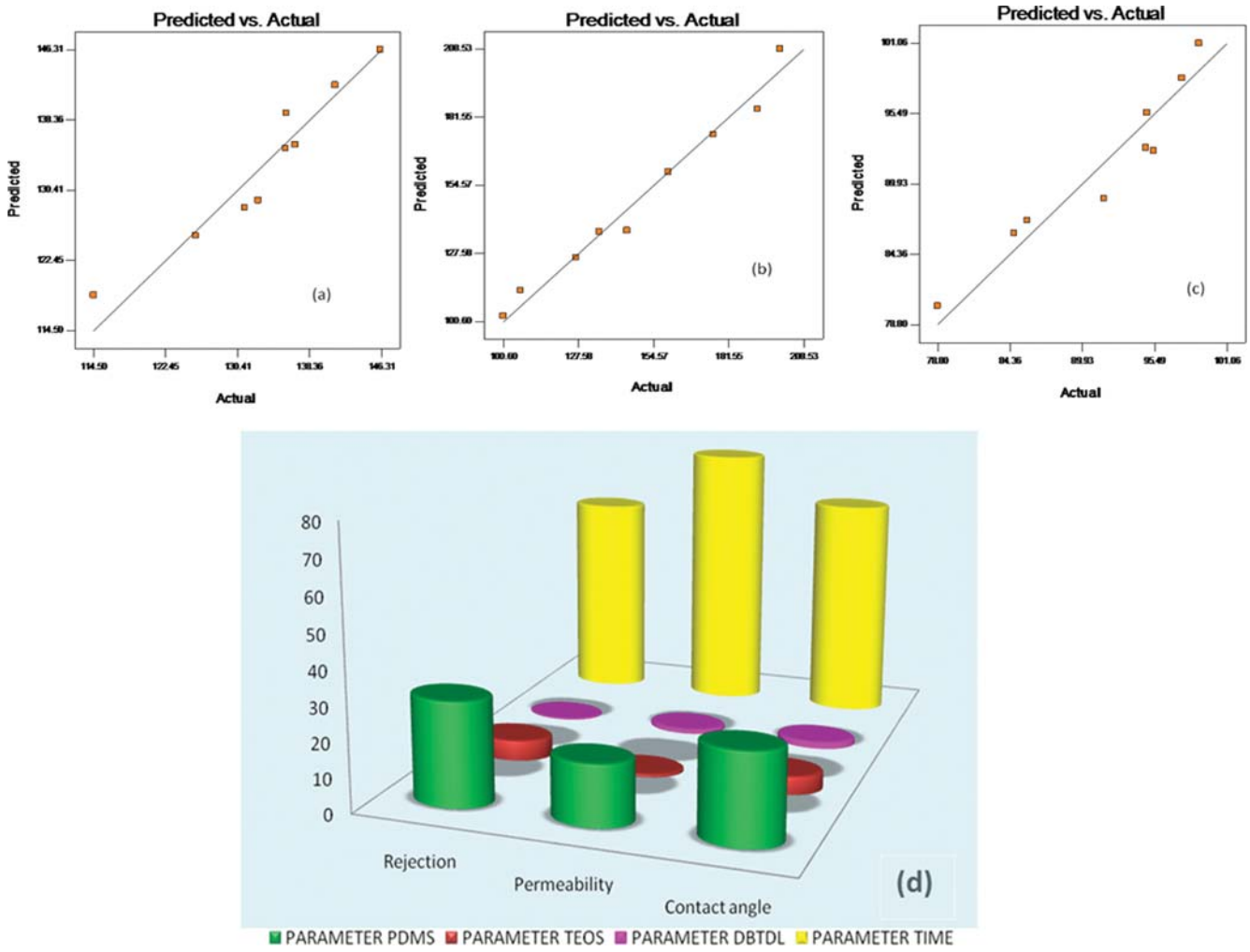

Fig. 2. Actual versus predicted plot of (a) contact angle, (b) clean water permeability, (c) ciprofloxacin rejection as obtained by Taguchi analysis, (d) Indicator of contribution of the factors upon response as obtained by ANOVA.

$h^{-1}bar^{-1}$ with small increase in contact angle from 131.2° to 135.8° (Table 3). This is clearly due to increased penetration of PDMS slurry in the porous support tubes and increase of interfacial membrane thickness. Similar effect was found for the coating time. For a particular PDMS concentration, increase in coating time from 2.5 to 7.5 min leads to increase in contact angle by 16° and reduction in clean water permeability by 86 $Lm^{-2}h^{-1}bar^{-1}$. Increase in cross-linkage between the PDMS and support tubes with increase in membrane thickness occurs with increasing coating time. Although statistical analysis shows negligible effect by TEOS, it restricts the swelling and mobility of the polymeric moiety, resulting in improved cross-linkage of the membranes [24]. The degree of cross-linkage varied from 93.7% to 99.4% upon variation of TEOS from 0.5 ml to 1.5 ml. Thus, to attain a highly cross-linked ceramic/PDMS composite membrane having high permeance and enhanced ciprofloxacin rejection properties, the coating parameters needed to be optimized.

Table 5 shows the optimum condition for attaining maximum ciprofloxacin rejection by keeping the coating parameters, concentration of the chemicals and coating time, within the experimental range as given in Table 1. The condition was selected based on maximum desirability and minimum usage of chemicals. The predicted values of Taguchi analysis show the hydrophobic membrane formed by slurry having composition of 5 ml PDMS (in 25 ml n-hexane), 0.04 ml TEOS, 0.02 ml DBTDL, 5 min coating time was highly efficient in removing 94.3% ciprofloxacin. Validation of the model predicted values was done by performing experiments at the same optimal conditions, and good similarity between them was found (Table 5). The hydrophobic membrane prepared under these conditions was used for further experimental study.

2. Preparation and Characterization of Hydrophobic Membranes

The underlying mechanisms responsible for adhesion of hydrophobic polymer PDMS to ceramic support are mechanical bonding, chemical bonding, surface adsorption, diffusion within the porous support [36]. The reasons have been explained sequentially [37]. The rough surface of the ceramic support tubes increases their interfacial contact area with the PDMS layer. This leads to enhancement of the capillary forces responsible for mechanical adherence of the PDMS film on the support tubes by dip coating process. Hydrogen bonding between the oxygen of PDMS and the -OH

Table 4. ANOVA of (a) contact angle (b) clean water permeability (c) ciprofloxacin rejection

Factors	Sum of squares (SS)	DOF	Mean square/ variance	F value	Prob>F	Percent (%)
(a) Contact angle (°)						
A	176.54	2	88.27	7.01	**0.04**	**26.4**
B	36.51	2	18.25	0.12	0.89	5.7
C	13.84	2	6.92	0.045	0.95	2.07
D	440.64	2	220.32	17.50	**0.01**	**66.01**
Residual	50.35	4	12.59			
Cor total	667.54	12				
(b) Clean water permeability ($Lm^{-2}h^{-1}bar^{-1}$)						
A	1812.91	2	906.45	15.09	**0.013**	**17.9**
B	97.15	2	48.57	0.02	0.98	0.96
C	143.12	2	71.58	0.029	0.97	1.41
D	8074.91	2	4037.45	67.22	**0.0008**	**79.93**
Residual	240.27	4	60.07			
Cor total	10128.08	12				
(c) Ciprofloxacin rejection (%)						
A	112.78	2	56.39	7.19	**0.04**	**30.42**
B	30.06	2	15.03	0.18	0.84	8.11
C	1.34	2	0.67	0.0078	0.99	0.36
D	226.51	2	113.25	14.43	**0.01**	**61.11**
Residual	31.39	4	7.85			
Cor total	370.68	12				

Table 5. Experimental and predicted values obtained under optimal conditions

Factors				Response		
A (ml)	B (ml)	C (ml)	D (min)	Contact angle (°)	Clean water permeability ($Lm^{-2}h^{-1}bar^{-1}$)	Ciprofloxacin rejection (%)
5	0.5	0.04	5	Predicted 136.7 Experimental 138.5	Predicted 124.7 Experimental 120	Predicted 94.3% Experimental 95.4

group of the hydrophilic support is responsible for chemical attachment. Adherence of the PDMS slurry to the surface occurs as it has much lower surface energy than the support tubes. An added advantage of clay-alumina based support is that swelling of the active separation layer of PDMS is restricted, making them stable for long-term, high pressure applications.

Stability of the PDMS membrane was increased by forming a cross-linked, three-dimensional network using TEOS in the presence of catalyst DBTDL. The main mechanism is hydrosilation reaction, proceeding via Chalk Harrod mechanism. The main stages involve formation of active species in the presence of catalyst in the induction period; the second phase corresponds to an exothermic region involving generation of the reaction products followed by slow termination of the reaction in the post curing stage [38-40]. The cross-linker concentration, the ratio of PDMS:cross-linker, cross-linking density, rate of hydrosilation reaction, type of catalyst, cross-linking time, cross-linking temperature are important factors to be considered to obtain stable, cross-linked PDMS membrane [38].

The PDMS film XRD in Fig. 3(a) shows the presence a large peak at 12.4° and small, broad peak at 22.4° which indicates tetragonal crystal lattice structure of PDMS film [24]. Thus, the reduced compactness in the PDMS film results in increased free volume, enhancing permeate flux of the composite membrane [41]. The clean water permeability of the composite membrane as calculated from the slope of permeate flux versus TMP plot was found to be 120 $Lm^{-2}h^{-1}bar^{-1}$ (Fig. 3(b)). The contact angle was 138.5°, showing highly hydrophobic surface (Fig. 3(c)). The results are in good agreement with the model predicted optimized findings as obtained by Design Expert.

Fig. 4(a) shows the FESEM image of the surface of the coated tubes. Uniform, defect-free PDMS separating layer was formed, reducing the pore size of the macroporous support tube. Incorporation of PDMS into the macropores of the support, with the appearance of wrinkles in the penetrated area is clear from the images. This is clear indication of constrained swelling effect of the polymer/ceramic composite membrane, as reported by Wei et al. [42]. The ceramic support restricts the release of the compressive strain generated, resulting in wrinkle formation. Fig. 4(b) represents the cross-sectional image of the membrane. Well defined interface

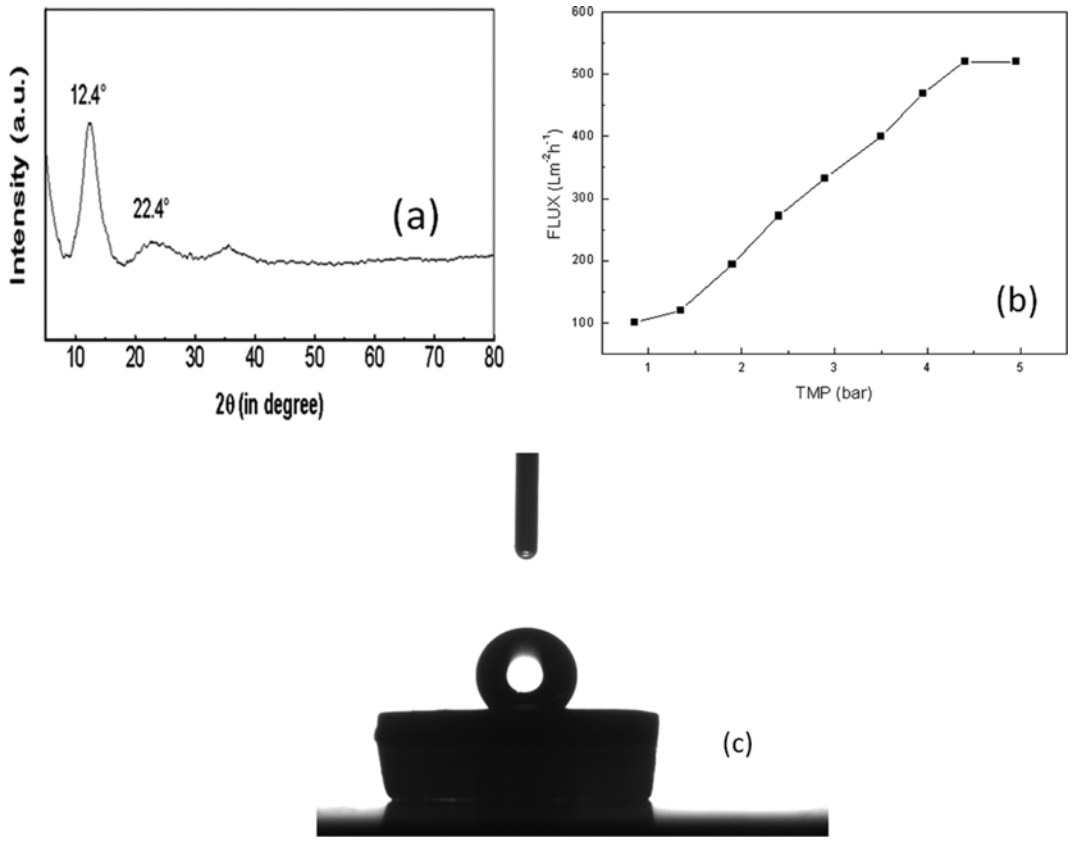

Fig. 3. (a) XRD of cross linked PDMS film, (b) clean water permeability, (c) contact angle of hydrophobic membrane.

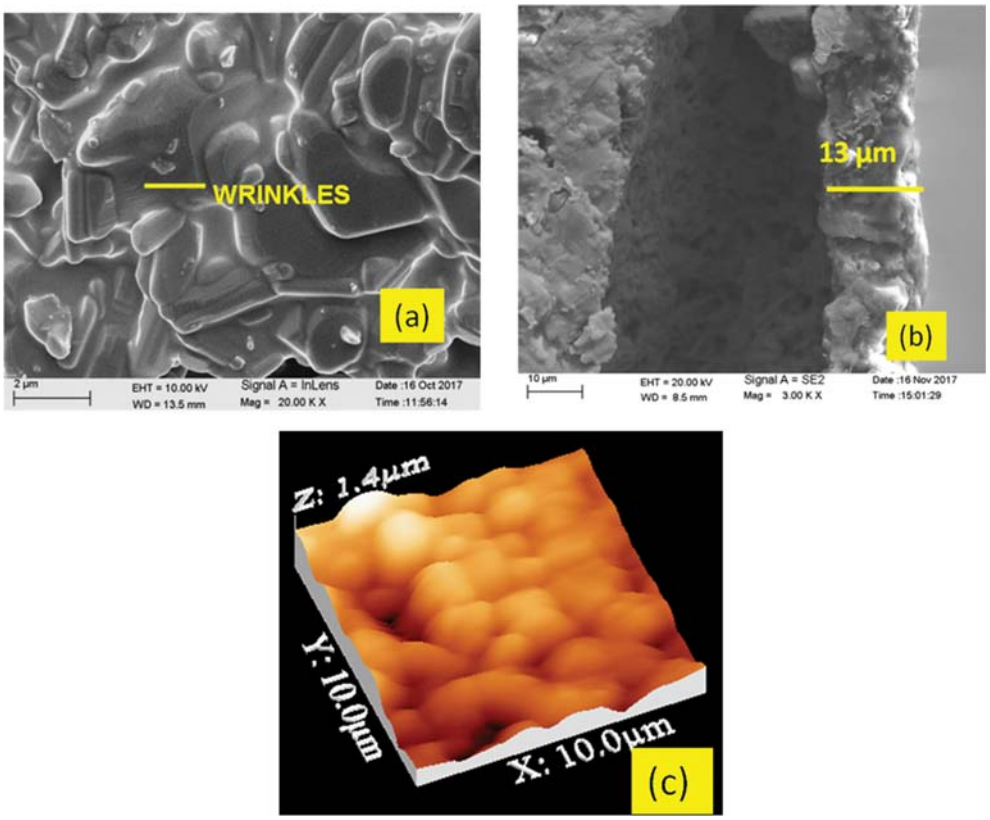

Fig. 4. FESEM of (a) surface, (b) cross-section, (c) AFM image of PDMS coated ceramic membrane.

between the support and membrane surface, both internal and external, has been clearly shown. The coating thickness was found to be 13 μm. The scanned area of 10 μm×10 μm in the AFM image (Fig. 4(c)) shows uniform surface with surface roughness of 0.167 μm.

The membrane showed negligible weight loss in the pH range of 2 to 11, indicating its stability. The degree of cross linking and swelling in neutral pH of water was found to be 98.5% and 0.2%, respectively. High degree of crosslinkage is attained by optimizing the concentration of the precursors and cross-linking time. Negligible swelling of the membrane is due to high degree of crosslinkage of PDMS film as well as ceramic macroporous support which restricts the motions of the polymer, resulting in constrained swelling of the membrane [42].

3. Filtration of Ciprofloxacin

3-1. Effect of Operating Parameters

The effect of operating parameters--CFV, TMP, filtration time--were investigated upon ciprofloxacin removal and permeate flux for the concentration range of 0.5 mg/L to 5 mg/L. Fig. 5 shows that increase in TMP leads to enhancement of permeate flux because membrane filtration depends on pressure gradient following Darcy's law. Rejection initially increases up to 3 bar, after which it decreases with increasing TMP. The maximum rejection was found to be 89%, 92.7%, 98.5% at 3 bar for feed concentration of 0.5, 1 and 5 mg/L, respectively. The initial increase in rejection may be due to convective transport of solute molecules from bulk solution to nascent membrane surface [43]. Moreover, with increasing TMP, higher permeate flux might result in dilution of the permeate stream. Hence, this dilution effect might be responsible for an apparent increase in rejection [44]. However, with further increase in TMP, increased penetration of ciprofloxacin molecules occurs, leading to their presence in the permeate stream, hence reducing the rejection [45]. Thus TMP of 3 bar was selected as optimum pressure for further filtration experiments.

CFV was varied from 1 L/min to 7 L/min at constant TMP of 3 bar. The CFV was found to affect the rejection and permeate flux in a synergistic way (Fig. 6). With increase in CFV, shear and turbulence at the surface of the membrane increases, which in turn helps to decrease the concentration polarization, causing increased permeate flux [46].

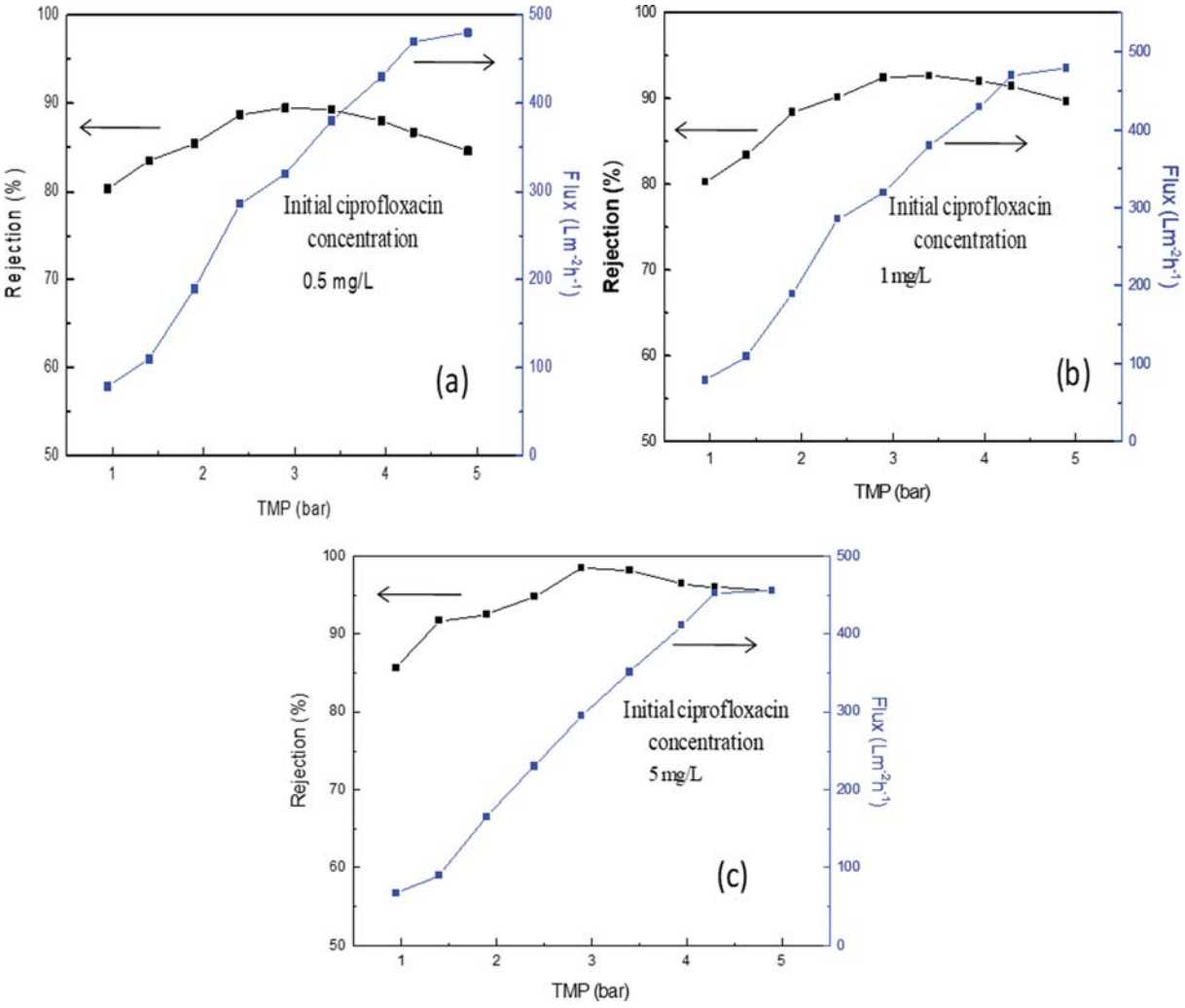

Fig. 5. Effect of TMP on flux and rejection of (a) 0.5 mg/L, (b) 1 mg/L, (c) 5 mg/L ciprofloxacin.

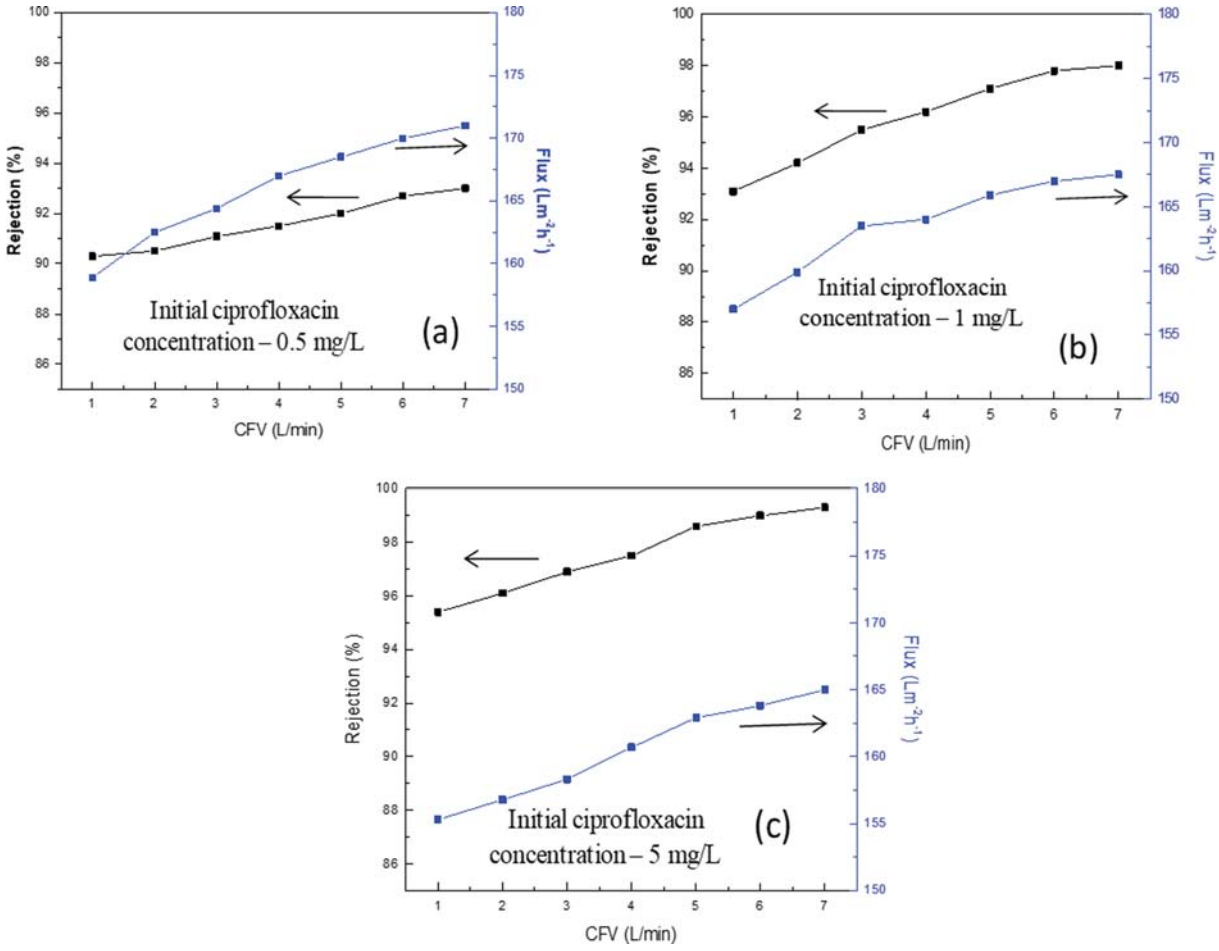

Fig. 6. Effect of CFV on flux and rejection of (a) 0.5 mg/L, (b) 1 mg/L, (c) 5 mg/L ciprofloxacin.

Ciprofloxacin filtration was performed for 3 h maintaining 3 bar TMP and 5 L/min CFV. Fig. 7 shows sharp increase in contaminant rejection with increasing time and it was maximized after 60 min of filtration. Maximum removal was 92.7%, 97.4% and 99.3% for 0.5, 1 and 5 mg/L feed solution, respectively. This was followed by a decreasing trend in rejection due to the concentration polarization effect, which causes increased chemical potential of the cake layer consisting of ciprofloxacin molecules [47] and hence their back diffusion from membrane surface to bulk solution. This membrane was highly efficient compared to the reported ones [22,48]. UF membrane with polyelectrolyte copolymer could remove about 80% ciprofloxacin at pH 5.0 [48]. About 95.7% ciprofloxacin with initial concentration of 10 mg/L was separated by NF90, a polyamide membrane due to the size exclusion, but the flux was as low as 24.39 $Lm^{-2}h^{-1}$ at the mentioned operating conditions [22].

Permeate flux also decreases gradually with increasing filtration time (Fig. 7) due to formation of cake layer on the membrane surface [46]. The flux decline was found to be about 9%, 18% and 23% after 3 h for 0.5, 1 and 5 mg/L, respectively. Increase in the ciprofloxacin concentration results in reduced flux due to concentration polarization. The adsorptive removal of the contaminant was confirmed by the experimental trend of decreasing rejection with decreasing feed concentration. Concentration gradient is the potential driving force for adsorptive process and hence this synergistic behavior.

To minimize fouling, for continuous operation, pneumatic backpulsing was applied at an optimized 30 min interval at 4 $kgcm^{-2}$ pressure for 1 min duration. Flux reduction reduced to 9.3%, 7.1%, 3.5% for 5, 1 and 0.5 mg/L, respectively (Fig. 8(a)).

After each filtration cycle, the membrane was cleaned with deionized water and the FFR was found to be 99.3%, 99.7% and 99.7% for 5, 1 and 0.5 mg/L, respectively. The robustness of the prepared membrane was judged in terms of the ciprofloxacin rejection after five cycles of filtration. It was found that rejection reduced by 2.1% only (Fig. 8(b)) proving long-term stability of the prepared hydrophobic membrane for removal of emerging organic contaminants.

3-2. Effect of Physico-chemical Property of Solute

The effect of feed solution pH on ciprofloxacin rejection was also investigated to find the effect of ionization states on rejection. Maximum rejection of 97.2% after 30 min, 97.5% after 60 min, 96.8% after 90 min of filtration was found for pH 4.5, 6.8, 9.5, respectively (Fig. 8(c)). Although the quantitative removal of the contaminant is almost similar, the time for attaining maximum separation becomes different. The probabilistic reason may be due to electrostatic interaction among negatively charged PDMS membrane and charged ciprofloxacin. At pH 4.5, strong affinity of the positively

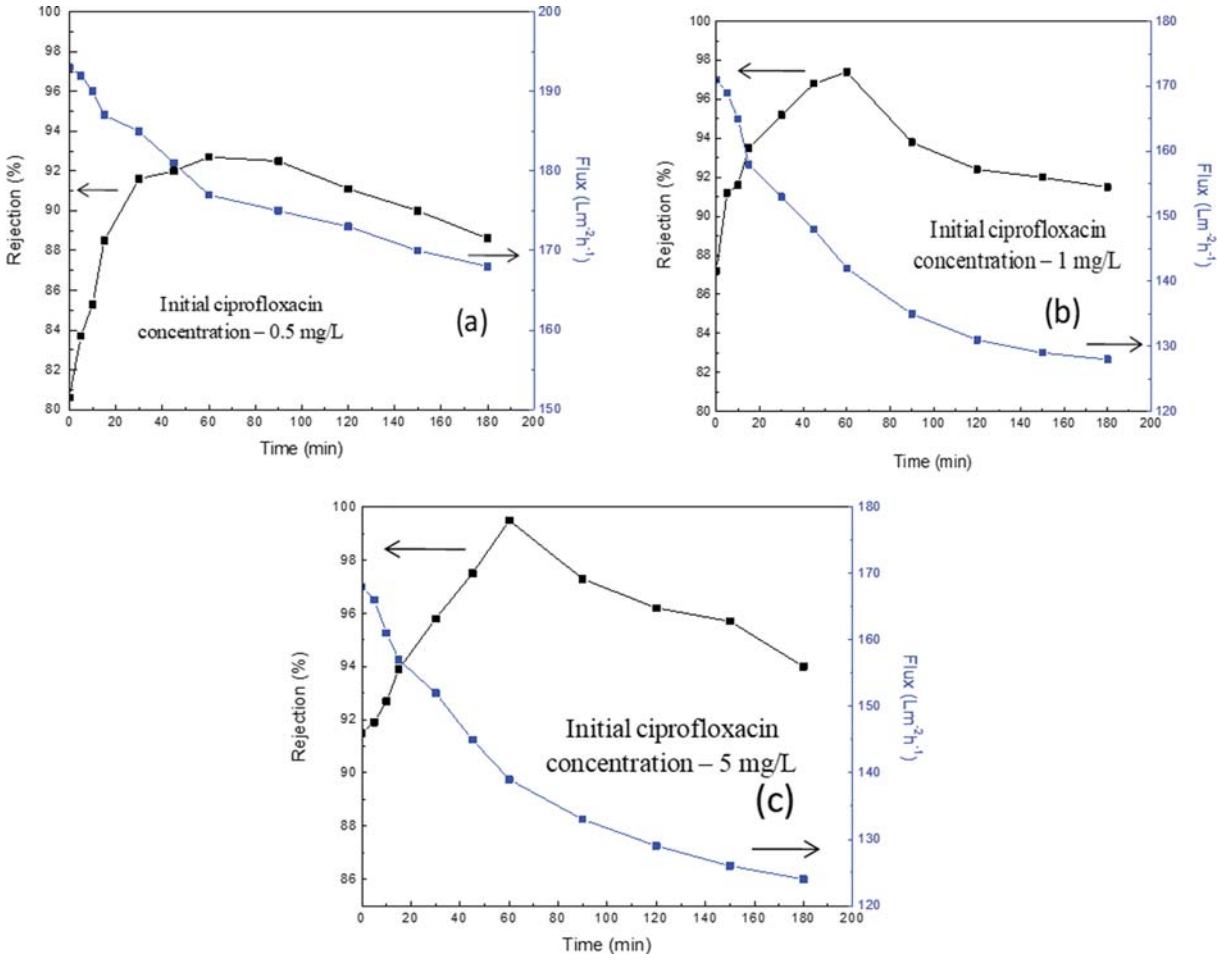

Fig. 7. Effect of filtration time on flux and rejection of (a) 0.5 mg/L, (b) 1 mg/L, (c) 5 mg/L ciprofloxacin.

charged molecule towards the membrane occurred, leading to efficient separation within 30 min of filtration. However, at 9.5, it exists as negatively charged moiety, resulting in repulsion from membrane surface. At the intermediate pH, the details of mechanism involved for removal have been discussed in the underlying section 3.4.

4. Mechanism of Ciprofloxacin Removal

Membrane based separation of the organic contaminants usually occurs via physical processes (size exclusion, steric hindrance, charge repulsion) and via chemical processes which includes hydrogen bonding, hydrophobic interaction, solvation energy. Ciprofloxacin is a moderately hydrophobic compound having Log K_{OW} of 1.9 [49]. Ciprofloxacin is reported to be highly adsorbed by PDMS [50]. When this target molecule comes in the vicinity of the active PDMS layer, different short range adsorptive forces like hydrophobic interaction, covalent bonding and electrostatic interaction come into action. Van der Waals π-π type interaction occurs between the electron-rich aromatic group of ciprofloxacin and vacant d-orbitals of siloxane in PDMS [49]. The bonding may occur via electron rich carboxylate group or the non-bonding, free electrons of the amine group. In such π-π type interaction, a dative covalent bond may be formed by transfer of electrons from highest occupied orbital to lowest unoccupied orbital of donor and acceptor, respectively [51]. The efficiency of the donor group increases with increase in aromatic rings due to enhancement of polarizability and increase in electron donating moieties. Similarly, with the increase in electron-deficient and electron-withdrawing groups, the acceptor ability is enhanced. Another probabilistic factor responsible for removal is hydrophobic interaction with the membrane surface. Hydrophobic compound ciprofloxacin forms a clathrate cage when present in water. This leads to decrease in entropy of the system. When such hydrophobic molecules are in contact with the hydrophobic membrane surface, rupture of the cage-like structure occurs and due to such interaction enthalpy, as well as, entropy of the process increases [52,53]. Thus, the main factor driving this spontaneous hydrophobic interaction involves reduction in the Gibb's free energy. The net free energy of the system due to solute-solvent, sorbent-solvent, sorbent-solute interactions is the driving force for the surface adsorption of ciprofloxacin from aqueous solution to active PDMS layer [54]. The surface roughness and thickness of the membrane coating also determined the availability of the sorption sites for the contaminant removal. Ceramic membrane with open porous structure was successfully modified to a hydrophobic, dense membrane with active coating thickness of 13 μm, enhancing physical adsorption of ciprofloxacin on its surface. Similar observations have been reported by other researchers

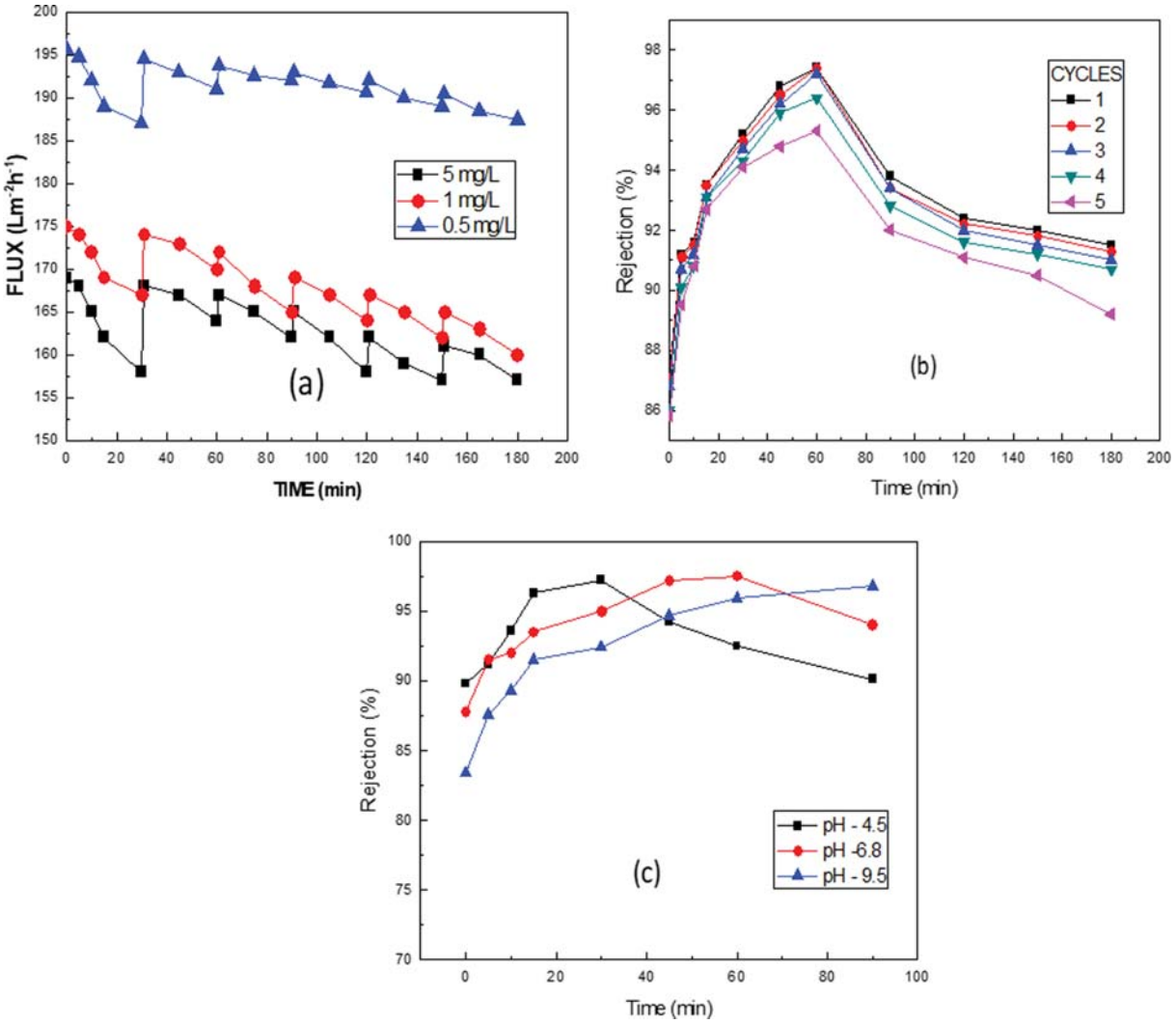

Fig. 8. (a) Effect of pneumatic backpulsing on permeate flux, (b) effect on time on rejection of ciprofloxacin after 5 cycles of filtration, (c) effect of pH on ciprofloxacin rejection.

[55,56]. Dip-coated PVDF membranes having coating thickness of about 10 μm was found to show higher separation efficiency for emerging contaminant compared to spray coated membranes with 2 μm thickness [55]. Electrostatic interaction among negatively charged PDMS membrane and charged ciprofloxacin molecule is also responsible for its removal at acidic and basic pH. The probable mechanism has been discussed in section 3.3.

Further confirmation of this adsorptive mechanism was carried out by performing a mass balance for the membrane filtration, considering amount of ciprofloxacin in the feed solution to be presented in the treated permeate, retentate and hydrophobic membrane surface (Eq. (2)). Accordingly,

$$C_f \times V_f = (C_p \times V_p) + (C_r \times V_r) + (C_m \times V_m) \quad (2)$$

where, C_f, C_p, C_m, C_r and V_f, V_p, V_m, V_r are the concentration and volume of ciprofloxacin solution in feed, permeate, hydrophobic membrane surface and retentate respectively.

Thus, ciprofloxacin retained by the membrane surface per unit area (A), after 3 h of filtration (M_{ads}) is given by Eq. (3):

$$M_{ads} = (C_f \times V_f) - [(C_p \times V_p) + (C_r \times V_r)/A \quad (3)$$

Obtained values of M_{ads} were 0.05 mg/cm^{-2}, 0.153 mg/cm^{-2}, 0.759 mg/cm^{-2}, respectively, for 0.5, 1 and 5 mg/L respectively.

5. Membrane Characterization Post Ciprofloxacin Filtration

Fig. 9(a) shows morphology of surface of PDMS membrane after filtration. FESEM images show that almost same structure is retained as the nascent membrane, without any solute deposition on the surface. Similar observation can be found from the AFM image (Fig. 9(b)), showing no definite changes in morphology of the PDMS membrane post filtration. Roughness was found to be slightly reduced to 0.106 μm due to deposition of solute contaminant particles during filtration, making the surface smoother compared to pristine membrane. Contact angle of the hydrophobic membrane after exposure in ciprofloxacin solution for 30 days was reduced to 135.3° (Fig. 9(c)). This shows stability of the hydrophobic membrane for filtration of the organic pharmaceutical component. FTIR study was performed upon the PDMS membrane in its pristine and post-filtration states to study and confirm removal of cipro-

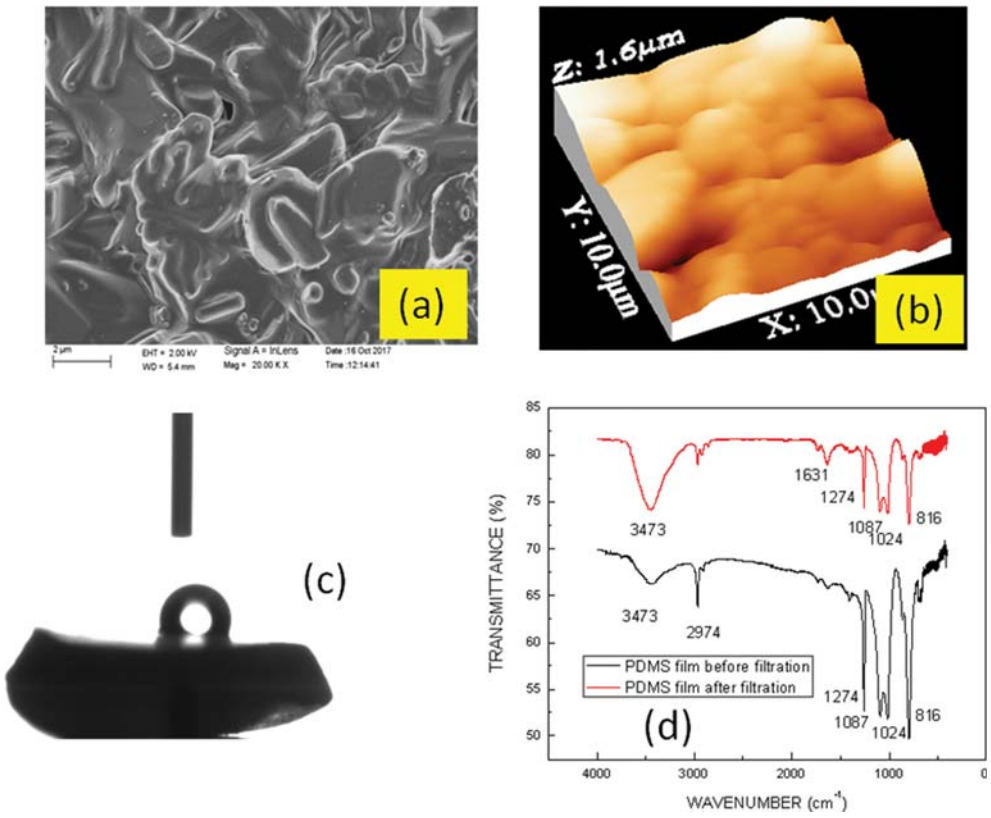

Fig. 9. (a) FESEM of membrane surface, (b) AFM of PDMS membrane, (c) contact angle of PDMS membrane post ciprofloxacin removal, (d) FTIR of PDMS membrane before and after removal of ciprofloxacin.

floxacin (Fig. 9(d)). Presence of peaks with unchanged intensity at 816, 1,024, 1,087, 1,274, 3,473 cm^{-1} was found for both for the PDMS membrane pre- and post filtration. Stretching vibration of -CH_3 group in Si-CH_3 resulted in characteristic peak at 816 cm^{-1}, Si-C, Si-O-Si stretching vibration gave rise to significant absorbance at 1,024 and 1,087 cm^{-1}, peak at 1,266 cm^{-1} signifies CH_3 deformation of Si-CH_3 group [57]. -CH_3 group in Si-CH_3 has asymmetric stretching vibration resulting in peak at 2,960 cm^{-1} and its subsequent decrease in intensity after adsorption due to participation of methyl groups in hydrophobic interaction [57]. Presence of a peak at 1,632 cm^{-1} is due to amine group of ciprofloxacin, which implies attachment of ciprofloxacin to the surface of PDMS.

CONCLUSION

Taguchi optimization process was successfully used to tailor the parameters for formation of PDMS/ceramic composite membrane, resulting in maximum contact angle and ciprofloxacin removal along with high flux. Relative contribution of independent factors--amount of PDMS, TEOS, DBTDL and coating time towards ciprofloxacin rejection--was 30.4%, 6.1%, 0.36%, 61.1% respectively. This shows coating time and PDMS dose have maximum effect upon the responses. The optimized preparation conditions (PDMS - 5 ml, TEOS - 0.4 ml, DBTDL - 0.02 ml and coating time of 5 min) resulted in hydrophobic membrane of contact angle 138.5° and clean water permeability of 120 $Lm^{-2}h^{-1}bar^{-1}$. The membrane resulted in ciprofloxacin rejection of 92%-99% for concentration ranging from 0.5 to 5 mg/L after 60 min of filtration at 3 bar pressure. The probable mechanism behind removal is van der Waals π-π interaction and hydrophobic interaction between solute molecule and membrane surface. Electrostatic interaction might also be a dominant factor when ciprofloxacin molecules exist in charged state. Application of pneumatic back pulsing for 1 min at 30 min interval with pressure of 4 $kgcm^{-2}$ helps to mitigate the permeate flux declination caused by concentration polarization. It resulted in about 53% reduction in flux decline for concentrated feed solution of 5 mg/L. Membrane characterization after five cycles of filtration showed negligible reduction in rejection of the contaminant and no significant changes in surface morphology as found from FESEM and AFM images. The present work thus emerges as an effective, sustainable way for remediation of emerging organic contaminants from wastewater.

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NOMENCLATURE

Symbol

A : membrane area [cm^2]
C_f : concentration of ciprofloxacin in feed [mg/L]
C_m : concentration of ciprofloxacin in hydrophobic membrane surface [mg/L]
C_p : concentration of ciprofloxacin in permeate [mg/L]
C_r : concentration of ciprofloxacin in retentate [mg/L]
M_{ads} : ciprofloxacin adsorbed by the hydrophobic membrane [mg/cm^{-2}]
V_f : volume of feed solution [L]
V_m : volume of solution in hydrophobic membrane surface [L]
V_p : volume of permeate solution [L]
V_r : volume of retentate solution [L]

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