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ARTICLE

Optimization of cleaning conditions on polytetrafluoroethylene (PTFE) microfiltration membrane used in treatment of oil-field wastewater

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Membrane fouling is one of the main drawbacks of microfiltration technology during the treatment of oil-field wastewater. To improve the overall efficiency requires a deep research on the optimization of membrane cleaning procedure. In this study, the effect of NaOH, NaOCl and HCl concentrations, soaking time and temperature on the flux recovery of PTFE membrane were investigated. Box-Behnken (BBD) coupled with Response Surface Methodology (RSM) was applied to provide clear understanding of the interaction between various process parameters. The process operating parameters were then optimized accordingly. The optimum conditions of NaOH, NaOCl, HCl, soaking time, and temperature were 1%, 0.72%, 0.65%, 3.35 h and 40.0 °C, respectively, under which flux recovery rate can reach 100%. In addition, analyses of field emission scanning electron microscopy (FESEM), fourier transform infrared (FTIR), atomic force microscopy (AFM) and contact angle (CA) reflected that the foulants accumulated on the membrane surface could be effectively removed at the optimum condition.

1.Introduction

As a by-product of the oil extraction process produced from oil rigs, oil-field wastewater severely pollutes environment (the soil, estuaries, rivers, lakes, even the air) for its high organic content as well as wastes crude oil and water resource, thus sewage needs to be treated before discharged to the environment.[1] Conventional techniques, such as gravity setting, incineration and dehydration, cannot effectively dispose emulsified and soluble oil in sewage.[2] In order to lessen this problem, membrane technology is by far widely applied due to its unique advantages including simple operation, chemical and thermal stability and without any phase change.[3,4] Among all these efficient methods, microfiltration (MF) is one of the most potential and essential membrane applications through sieving mechanism with distinct pore sizes to retain particles larger than the pore diameter (0.1 to 10 μm) in the process of oil/water separation.[5] Polytetrafluoroethylene (PTFE) membrane, a new type of microfiltration membrane, has a lot of advantages such as uniform aperture, stable performance, high mechanical strength, excellent resistance of acid and alkali, microorganism, oxidizability, oil and pressure and so forth. However, it has been mainly used in the fields of proton exchange membrane fuel cells and membrane distillation since it was produced,[6-9] It is envisioned that if the application of PTFE membrane in treating oil-field wastewater is developed, the range of its employment would be enlarged.

Nevertheless, a major obstacle to the widespread expansion of membrane technology implementation is related to membrane fouling, which is unavoidable during the filtration process.[10,11] The flux decreased by fouling leads to an increase in transmembrane pressure, resulting in membrane degradation on account of the frequency and harshness of cleaning/disinfection conditions. Three main factors exist regarding the fouling mechanisms of the microfiltration (MF), i.e. pore blocking, cake formation and the adsorption of the fouling materials.[12,13] Furthermore, membrane fouling depends on several influence factors, such as membrane morphology, the feedwater composition, the particle size distribution, the organic matter load and the operating conditions and so forth.[14,15]

If fouling remains an inevitable issue, membrane cleaning is considered as a compulsory procedure during the filtration operation so as to regain membrane flux and performance.[16] Cleaning is usually conducted in four forms: enzymatic, biological, chemical and physical. Among these methods, chemical cleaning has been correspondingly demonstrated to be satisfactory of recovering membrane flux by removing impurities in terms of chemical agents in previous studies.[17,18] To find appropriate materials as detergent is necessary. This step depends on feed composition and precipitated layers on the membrane surface and a trial and error method shall be carried out in most cases.[19] Characteristically, the favorable cleaning reagents should be safe, inexpensive, stable chemically, and be able to be washed with water, to avoid new fouling, as well as be able to loose and dissolve most of

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the sediments from the surface of membrane with no surface damage.[20] Different means for the cleaning agents to affect the present of foulants on membrane surface are as follows: contaminants may be removed, morphology of precipitates may be altered (swelling, compaction) and/or surface chemistry of deposit may be changed, and the possible reactions may occur, such as saponication, solubilisation, dispersion (suspension), hydrolysis, peptization, and chelation.[21] The mechanism of cleaning is primarily electrostatic repulsion. An increase in electrostatic potential through charge density, polarity or pH of the cleaning solution can suppresse the attraction forces and then increase the cleaning efficacy.[22]

Response surface methodology (RSM), allowing for a reduction in the number of experimental trials, has been proved to be an effective technique for modeling, evaluating and optimizing the problems in which a response of interest is influenced by several variables.[23,24] Takuro et al have applied RSM to achieve satisfactory responses of lateral flow membrane performances.[25] Xiarchos et al. have used RSM as the experimental method on micellar-enhanced ultrafiltration during the separation of copper from aqueous solutions.[26] As discussed above, there are numerous containable factors in membrane cleaning. Accordingly, Box-Behnken (BBD), a method of RSM, was applied in the present study to determine the effects and interactions of these factors on the flux recovery rate of PTFE membrane. In addition, the primary objective is to acquire the optimum conditions for membrane cleaning that can be virtually applied to microfiltration systems which is operated in treatment of oil-field wastewater to restore or maintain the performance of the membrane in terms of its permeability and protect the equipment.

2.Materials and methods

2.1. Membrane

Polytetrafluoroethylene (PTFE) membrane manufactured by VALQUA Industries (Japan) was used in all the experiments. The membrane consisted of a polytetrafluoroethylene layer on a polyethylene terephthalate (PET) support with a standardized pore size of 0.1 μm. It had an effective area of 0.05 m^2 (single side), with an external diameter of 290 mm and a working width of 180 mm.

2.2. Experimental setup

In the experimental trials, the crossflow batch process was selected. A wastewater treatment MF apparatus was installed at the Water Agencies in Daqing (China) and the experimental setup was schematically shown in Fig. 1. A 0.06125 m^3 reactor with aerator was fed with wastewater pre-treated by coagulation, airfioatation, advanced oxidation and sand leach in sequence. The pH and the temperature of the feed were 11.7 and 40 °C, respectively. A detailed characterization of feed water was presented in Table 1. A 0.018 m^3 membrane tank equipped with a PTFE flat sheet membrane was set in the upper part. The operating cycle was: 9 min filtration, 1 min interval, 60 min backwashing cycle, 1 min backwashing. To achieve the membranes fouled in same condition, the operating flux and backwashing flux were kept at a constant value of 10 $L/m^2 \cdot h$ and 90 $L/m^2 \cdot h$, respectively, and the intensity of gas washing was 10 $m^3/m^2 \cdot h$. The microfiltration process was terminated when transmembrane pressure (TMP) reached the predetermined value (80 kPa), which was recorded automatically through the data acquisition system.

Table 1 Composition of feed water

Component	Concentration (mg/L)
Median particle diameter (μm)	5.59
Oil	6.64
Suspended solid	83
TOC	1083
APAM	749
Surface active agent	37
CODcr	1305
Turbidity	16.4
Carbonate	1925
Bicarbonate	2890

2.3. Experimental design

The experiments were designed using Design of Experiment Software Version 8.0.5b (Stat-Ease Inc., USA). The software was employed to optimize the effects of important process parameters for the flux recovery of PTFE membrane, namely concentrations of NaOH, NaOCl and HCl, soaking time and temperature. It is noteworthy to mention that several optimization methods such as Full Factorial Design, Box-Behnken, and D-optimal Designs etc. are used to optimize the process. In this study, Box-Behnken (BBD) coupled with Response Surface Method (RSM) was selected. The flux recovery was the response. The coded and actual levels of the variables were shown in Table 2. The process parameters were NaOH 0.1~1%, NaOCl 0.1~1%, HCl 0.1~1%, soaking time 0.5~5 h, temperature 30~50 °C. The coded values were designated as −1 (low) and +1 (high). The levels of each process operating parameter were chosen based on the previous literatures.[27,28] To provide a true measure of error due to the natural variations, six replicated center points were conducted in randomized order and the practical flux recovery rates at different cleaning conditions according to the complete design matrices were exhibited in Fig. 2. The relationship between dependent and independent parameters

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in this study is explained by the following second-order polynomial model:

$$Y = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + \sum b_{ii} x_{ii}^2 \quad (1)$$

where x_i are the input variables impact the response variable Y, b_0, b_i, b_{ii} and b_{ij} are the regression coefficients.

Table 2 Experimental parameters and levels of Box-Behnken Design

Coding	Variable	The coding level	
		-1	+1
X_1	Concentrations of NaOH	0.1	1
X_2	Concentrations of NaOCl	0.1	1
X_3	Concentrations of HCl	0.1	1
X_4	Soaking time	0.5	5
X_5	Temperature	30	50

2.4. Analytical methods

Oil and APAM content were analyzed by a UVspectrophotometer (UV2550, Shi madzu, Japan). Turbidity was measured by a turbidimeter (TURBO550, WTW, Germany). A TOC analyzer (TOC-VCPH, SHIMADZU, Japan) was employed to determine total organic carbon (TOC). To identify the microstructure of the contaminated membrane and to determine the surface morphology of PTFE membrane, a field-emission scanning electron microscope (FESEM; S-4800, Hitachi, Japan) equipped with energy dispersive X-ray spectrometer (EDX; KEVEN, USA) and atomic force microscopy (AFM; Digital Instruments, Veeco, USA) were utilized, respectively. To observe the chemical composition of pollutants on the membrane surface, spectra was collected with a Nicolet 8700 Fourier transform infrared spectrum spectrometer (FT-IR; Thermo, USA). Dataphysics OCA-15plus (DataPhysics, USA) was utilized to measure membrane contact angle using the sessile drop method.

To monitor the performance as a reference and efficiency of the membrane cleaning process, the membrane was thoroughly rinsed with ultrapure water and the flux of which was measured after each trial at a temperature of 40 °C, trans-membrane pressure (TMP) of 10 kPa. The value of flux recovery (FR) was calculated by:

$$W_{FR} = \frac{F_c - F_p}{F_i - F_p} \times 100\% \quad (2)$$

where W_{FR} is flux recovery (%), F_c is permeate flux after chemical cleaning (L/m^2· h), F_p is permeate flux after pollution (L/m^2· h), F_i is initial permeate flux (L/m^2· h).

3.Results and discussion

3.1. Model fitting and analysis of variance (ANOVA)

A second-order polynomial model was used to fit the experimental data obtained from the statistically designed experimental conducted by Box-Behnken design and to predict the flux recovery of PTFE membrane within the limits of experimental parameters in terms of coded factors (in Eq. 3):

$$y=94.90+2.39X_1+9.48X_2+0.79X_3+12.31X_4+1.26X_5-2.10X_1X_2-2.18X_1X_3+1.18X_1X_4-0.66X_1X_5-0.40X_2X_3-4.45X_2X_4-1.41X_2X_5-0.83X_3X_4+0.97X_3X_5-1.70X_4X_5-1.81X_1^2-4.58X_2^2-0.82X_3^2-9.95X_4^2-0.76X_5^2$$

$$R^2=0.9968 \quad (3)$$

Subjected to: $-1 \le X_i \le +1$, for i = 1, 2, 3, 4, 5

Eq. (3) made a good visualization of effects of significant factors and their interactions on response. High value of determination coefficient (R^2=0.9968) suggested that the model was able to explain more than 99% of the variation of the response as a function of the variables. The fitting results of the second-order response surface model in the form of ANOVA at 95% level of confidence were shown (Table 3). It should be noted that only the parameters with significant values were reported in Table 3. The model F value of 385.87 implied that most of the variations in the responses were explained by the regression equation, and high F-value together with the low value of P ($P < 0.0001$) pointed out the high significance of the fitted model. In general, the larger the F-value and the smaller the P-value, the more significant is the corresponding coefficient.[29] Accordingly, detailed scrutiny of the Analysis of variance (ANOVA) revealed that X_1, X_2, X_4 and X_5 were statistically significant for the

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response, while X_1X_2, X_1X_3 and X_2X_4 were highly influential secondary interactions on the flux recovery. The positive sign in front of the terms shows synergistic effect while the negative sign indicates antagonistic effect.[30]

The normal probability plot of the residuals and the residuals versus the predicted response were shown in Fig. 3. As shown in Fig. 3 (a), the residuals generally fell on a straight line suggesting that errors were normally distributed and independent of each other. This also suggested that the error variances were homogeneous and the residuals were independent, supporting adequacy of the least-square fit.[23] As can be seen from Fig. 3 (b) and (c), residuals were equally scatter about the x-axis with disorder structure and vague pattern implying that the proposed model was adequate and no reason to suspect any violation of the independence or constant variance assumption.[26] Fig. 3 (d) showed that the points or point clusters were placed very close to the diagonal line as a result of their low discrepancies, indicating a good fitness to the experimental data in different conditions for the response model. Hence, the model was considered adequate to predict the actual flux recovery in the limits of the experimental factors..

Table 3 ANOVA table for quadratic polynomial model (response: flux recovery rate of PTFE membrane)

Source	Quadratic sum	Degree of freedom	Mean square	F value	P value	significant
Model	5132.79	20	256.64	385.87	<0.0001	significant
X_1	91.58	1	91.58	137.70	<0.0001	significant
X_2	1438.87	1	1438.87	2163.41	<0.0001	significant
X_4	2426.06	1	2426.06	3647.69	<0.0001	significant
X_5	25.48	1	25.48	38.31	<0.0001	significant
X_1X_2	17.68	1	17.68	26.59	<0.0001	significant
X_1X_3	19.10	1	19.10	28.71	<0.0001	significant
X_2X_4	79.30	1	79.30	119.23	<0.0001	significant
X_1^2	28.64	1	28.64	43.07	<0.0001	significant
X_2^2	183.40	1	183.40	275.75	<0.0001	significant
X_4^2	863.15	1	863.15	1297.79	<0.0001	significant
Lack of fit	10.22	20	0.51	0.40	0.9355	not significant

3.2. The effects of factors on flux recovery

3.2.1 Effect of concentration of NaOCl and soaking time. The plot for response surface depicted the effects of NaOCl concentration and soaking time on flux recovery of PTFE membrane (Fig. 4). From Fig. 4, it could be seen that the flux recovery was low when soaking time was short. Moreover, the response value was increased to some extent by prolonging the process time. This trend can be reversed when soaking time was higher than 4.1 h. Besides, an increase in concentration of NaOCl led to large flux recovery of PTFE membrane within certain limits. For instance, the concentration of NaOCl in coded (+1) yielded higher flux recovery (98.47%) than 83.93% in coded (-1) when other parameters remained constant. These results are supported by previous work in which NaOCl exhibited an effective cleaning performance for a cross-flow microfiltration membrane fouled by microalgal biomass.[31] Likewise, Liang et al. [32] and Kwon et al. [33] observed that NaOCl was an effective detergent during membrane cleaning process. The ability of NaOCl through several mechanisms as follows to act as a swelling agent and protein solubilizer, in addition to its capability to break the chemical bonds between the membrane and its foulants: (i) increase ionic strength; (ii) increase the solubility of organic pollutants; (iii) increase pH, which results in increasing negative charge of organic matter due to deprotonation of carboxylic and phenolic substances. [34, 35] APAM, one of the main ingredients in the wastewater, was degraded by reacting with NaOCl accoding to the chemical reactions (4) to (8), which can be summarized to 3 phases, namely (1) chlorination of nitrogen ion in acylamino; (2) detachment of hydrogen ion and rearrangement of N-chlorinated anion; (3) conversion of formyl in polymer into amidogen.[36] Besides, as shown in Fig. 4, the response was significantly affected by the interaction between concentration of NaOCl and soaking time. This observation

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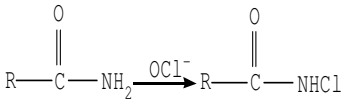
was confirmed by the quadratic polynomial equation since the interaction constant coefficient of these two variables is the most obvious among the interaction terms.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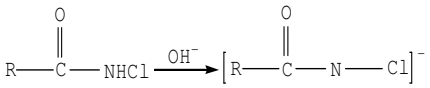
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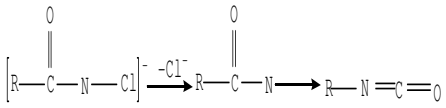
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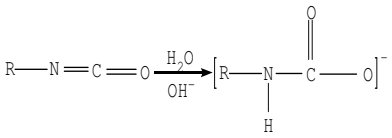
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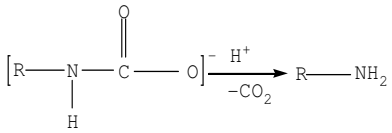
(8)

3.2.2 Interactions between concentrations of NaOH, NaOCl and other factors. The interactions of concentration of NaOH, NaOCl and other factors were expressed as two-dimensional plots (contour plot) and three-dimensional plots (response surface) and shown in Fig. 5. Under the low soaking time, the flux recovery improved indistinctively with the increasing concentration of NaOH (Fig. 5a). Moreover, when soaking time was extended with higher NaOH concentration, an enhancement of the response value to a certain degree can be observed. NaOH solutions wash away organic-fouled membranes by means of hydrolysis and solubilization. The caustic cleaning was deemed to be effective in removal of the organic foulants. This was owing to the presence of hydroxyl ions in alkaline solutions that promote disruption of the foulant layer by the mechanisms stated in Section 3.2.1. However, the effect of concentration of NaOH on the response was not as significant as that of soaking time on it. For example, when kept X1 in coded (-1) and other factors in center point constant, the flux recovery of PTFE membrane increased from 69.63% to 91.35% with soaking time ranging from 0.5 h to 5 h. Compared with NaOH solution, NaOCl displayed a higher cleaning efficiency (Fig. 4 and Fig. 5 (a)), which was supported by similar studies.[31, 37]

The effects of temperature associated with various concentrations of NaOH and NaOCl on the response were investigated. As can be seen clearly in Fig. 5 (b) and (c), the reciprocities of temperature and other two factors were not remarkable. The smaller interaction constant coefficients of X_1X_5 and X_2X_5 in Eq. 3 can be used to account for the conclusion. Normally, enhancement of temperature from 30 °C to 40 °C raised the cleaning efficiency when kept other parameters invariable. Temperature improves the efficiency of membrane chemical cleaning by changing the equilibrium constant of the reaction and the reaction kinetics, as well as changing the solubility of fouling aterials and/or reaction products.[38] However, further augment in temperature deteriorated the rate of flux recovery.It is therefore possible that the higher temperature can lead to a greater disintegration or solubilization of the deposit and a change in the polymeric structure of the PTFE membrane.

3.2.3 Interactions between concentration of HCl and other factors. An increase in concentration of HCl improved the cleaning performance within certain limits. For instance, the response value increased from 86.65% to 93.36% when concentration of HCl increased from 0.1% to 1.0% with no variation of other factors, a change of +6.67% (in Run 23 and 29). This indicated that HCl is suitable for the removal of inorganic pollutants on the membrane. In related study, AL-Amoudi also observed that higher flux (9.2 kg/m^2· h) was achieved by treating the membranes with HCl compared to an untreated membrane flux (5.6 kg/m^2· h).[39] However, this effect of HCl on the flux recovery of PTFE membrane is less significant than that of NaOH and NaOCl on account of the smaller coefficient sign in Eq. 3. These observations were supported by Norazman et al., who found that lower flux recovery and resistance removal of membranes cleaned with HCl than that of NaOH.[40] Fig. 6 (a) to (d) showed that the mutual effect on the response between concentration of HCl and NaOCl was more significant than that of between HCl and other three factors.

3.3. Optimization and validation

The optimized cleaning condition of PTFE membrane was obtained by seeking the extremum of regression model. And it revealed that the optimal condition were NaOH 1%, NaClO 0.72%, HCl 0.65 %, soaking time 3.35 h and temperature 40.0°C. Accordingly, a predicted maximum response value of 99.56% existed. To test and verify the fitted model, the validation experiments were conducted. Consequently, the average experimental flux recovery of the fouled membrane was 100% after cleaning thoroughly, which was in close proximity to the predicted value. It is worth mentioning that the regression equation can be predicted reasonably and optimized the cleaning condition of PTFE membrane.

3.4.Morphology of PTFE flat membranes

The morphology and structure of the virgin, fouled and cleaned membranes under the optimum condition were inspected by SEM analysis and illustrated in Fig. 7. The new membrane has a rough, albeit relatively flat, surface with irregular pores (Fig. 7a). However, as shown in SEM graph in Fig. 7b, the fouled membrane surface was covered with a thin smooth pollutant layer, and most of pores were clogged, indicating that the reduction in the flux recovery was mainly due to the block of membrane pore by the formation of fouled layer, a thickness of about 4 μm. Fig. 7c represented membrane surface after cleaning under the optimal operating condition. Removal of most of the deposited contaminants from the membrane surface was clearly observed, suggesting

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that the membrane surface have returned to be harsh quite similar to the virgin membrane and the pores became distinct again.

EDX analysis (Table. 4) of the fouled membrane surface demonstrated obviously the main elements of pollutants were carbon and oxygen which could be attributed to organic matters in the effluent, i.e. the petroleum pollutants and polymer in the wastewater. The existence of Fe, Ca, Si and Cu elements were due to minerals in the rock swelled and developed to suspended solids during the formation process of oil extraction wastewater. The iron and silicon on the membrane were the main inorganic pollutants, with the mass percent comparatively higher than that of calcium and copper. In addition, a lot of OH- in oil-field water, suggesting that the inorganic pollutants were likely to be SiO_2, $Fe(OH)_3$, $CaCO_3$, $MgCO_3$. Trace amounts of sodium element (2.11%) were assigned to detergent of NaOH adsorbed on the fouled membrane surface.

Table 4 EDX analysis of membrane surface of virgin, fouled and cleaned membranes

Elements	Mass percent of virgin membrane (%)	Mass percent of fouled membrane (%)	Mass percent of fouled membrane after cleaning (%)
C	28.26	38	28.38
O	6.68	14.02	6.74
F	65.06	17.44	64.41
Cu	0.00	1.01	0.00
Na	0.00	2.11	0.47
Mg	0.00	0.37	0.00
Al	0.00	0.38	0.00
Si	0.00	9.54	0.00
Cl	0.00	0.86	0.00
K	0.00	0.59	0.00
Ca	0.00	2.12	0.00
Fe	0.00	13.55	0.00

3.5. FTIR analysis

As shown in Fig.8 (a and c), the band intensities of the fouled membrane was significantly sharpened in comparison with that of the original membrane, with some new bands appeared due to the coating of foulants. The strong absorption bands at 3285 cm^{-1} and 1550 cm^{-1} were both attributed to nitrogen-hydrogen bond. Moreover, these peaks were closely related to polyacrylamide by measuring the composition of feed water and molecular formula of polyacrylamide. Several typical absorption peaks of functional groups indicated the existence of many important petroleum contaminants. For instance, the appearance of the characteristic bands detected at both 2923 cm^{-1} and 2853 cm^{-1} were believed to be attributed by carbon-hydrogen bond, while the presence of the peak of 1641 cm^{-1} were assigned for carbon-carbon double bond, and 1203 cm^{-1}, 1144 cm^{-1} and 1044 cm^{-1} represented carbon-oxygen-carbon,carbon-oxygen, carbon-oxygen-carbon, respectively. Generally, the differences in pattern between the recorded spectra indicated the changes in chemical composition of cleaned and virgin membranes (Fig.8c) whereas it became negligible after the cleaning procedure (Fig. 8b), which was quite similar to the virgin condition (Fig. 8a). This result provided implications about the high efficiency of the cleaning methods.

3.6. Three-dimensional AFM observation for the surface of the membranes

Three-dimensional AFM images were applied to determine the morphological changes of the fouled PTFE membrane before and after chemical cleaning. By comparing the new membrane (Fig. 9a) with the fouled membrane (Fig. 9b), it could be found that the surface of virgin membrane was accidented and undulated, which exhibited a higher topography than the fouled membrane. After subjected to microfiltration with the wastewater, the surface morphology of the membrane became relatively flat and smooth. However, after cleaning at the optimum condition, the surface of the fouled membrane restored the surface morphology (Fig. 9c), which was akin to the original membrane. It can be inferred from SEM and AFM that combination of cleaning agents including NaOH, NaOCl and HCl under appropriate soaking time and temperature was able to remove a portion of the cake layer on the surface.

3.7. Other changes in membrane surface characteristics

One of the major surface properties analyzed to learn alteration of the membrane surface characteristics is contact angle, which is a reflection of the hydrophobic/hydrophilic character of the membrane. [27] The contact angles of virgin, fouled and cleaned membranes were displayed in Table 5. The contact angle of the virgin membrane (120.1°) revealed that PTFE membrane is quite hydrophobic. In comparasion to the virgin one, the variation of contact angle of fouled membrane comparing to the virgin one was insignificant although fouled membranes became somewhat hydrophilic due to the relatively hydrophilic nature of foulants. After chemical cleaning, contact angle of the fouled membrane restored nearly close to that of the original one. Moreover, it turned out that there was no distinction between the virgin membrane and the cleaned one in both pore size and tensile strength.

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Table 5 Changes in contact angle, pore size and tensile strength of PTFE membrane surface

Classification	Contact angle	Pore size (μm)	Tensile strength (MPa)
Virgin membrane	120.1°	0.1013	15.5
Fouled membrane	127.3°	——	15.6
Cleaned membrane	120.9°	0.1033	15.5

3. Conclusion

(1) The application of Box-Behnken Design (BBD) coupled with Response Surface Methodology was found to provide clear understanding of the interactions between various process parameters (concentrations of NaOH, NaOCl, HCl, soaking time and temperature) for the cleaning procedure of PTFE membrane.
(2) Analysis of variance (ANOVA) further corroborated the authenticity of the polynomial models in pristine prediction of response. The values of the model statistics indicated the precision of the fitted empirical models in response determination.
(3) In the range of the considered factors, the optimum condition was found to be (NaOH 1%; NaOCl 0.72%; HCl 0.65%; soaking time 3.35 h; temperature 40.0 °C). It was verified that the actual average experimental flux recovery of the fouled membrane after cleaning was 100%, in close proximity to the predicted value (99.56%).
(4) The morphology and structure of the virgin, fouled and cleaned membranes under the optimum condition were inspected using SEM and AFM analysis and moreover, removal of most of the deposited contaminants on the membrane surface was clearly observed.
(5) FTIR analysis was carried out for qualitative analysis of the pollutants on the surface, and the results indicated the high efficiency of the cleaning procedure.
(6) The contact angle of the virgin membrane (120.1°) revealed that PTFE membrane was quite hydrophobic. The variation of contact angle of fouled membrane compared with the new one was not significant.

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Figures:

Fig. 1 The schematic of the experimental apparatus

Fig. 2 The practical flux recovery rate at different cleaning conditions

Fig. 3 Residuals plots (a, b, and c) for the BBD design and the relationship of predicted and actual value (d)

Fig. 4 Plots for contour and response surface presenting the effects of concentration of NaOCl (%) and soaking time (h) on flux recovery by chemical cleaning: (a) contour plot (2D); (b) response surface 3D

Fig. 5 Plots for contour and response surface presenting the interactions between concentrations of NaOH, NaOCl and other factors on flux recovery: (a) contour plot of concentration of NaOH and soaking time (2D); (b) response surface of concentration of NaOH and soaking time (3D); (a) contour plot of concentration of NaOH and temperature (2D); (d) contour plot of concentration of NaOCl and temperature (2D)

Fig. 6 Plots for contour presenting the interactions between concentrations of HCl and other factors on flux recovery: (a) contour plot of concentration of HCl and NaOH (2D); (b) contour plot of concentration of HCl and soaking time (2D); (c) contour plot of concentration of HCl and NaOCl (2D); (a) contour plot of concentration of HCl and temperature (2D)

Fig. 7 SEM images of surface of (a) original membrane, (b) fouled membrane, and (c) fouled membrane after cleaning under optimum operating condition

Fig.8 FT-IR spectra of original membrane (a), fouled membrane after cleaning (b) and fouled membrane (c)

Fig. 9 Three-dimensional AFM images of surface of (a) original membrane, (b) fouled membrane, and (c) fouled membrane after cleaning.

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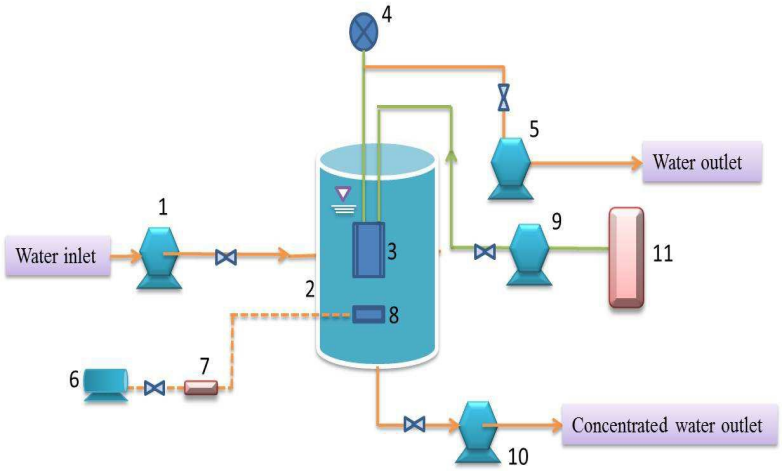
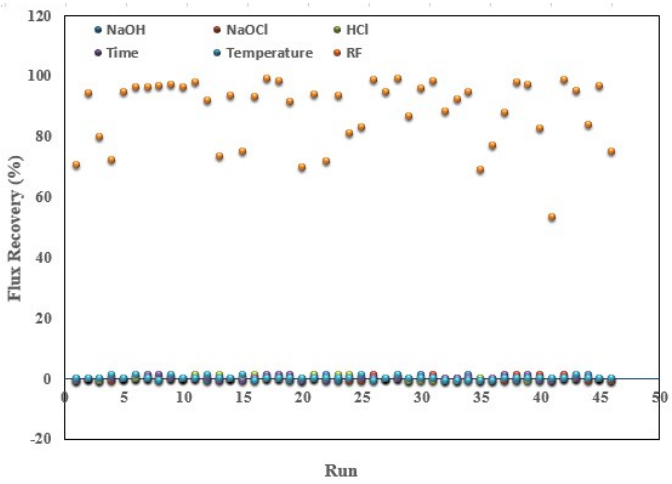


1 pump 2 feed tank 3 membrane module 4 pressure gauge 5 constant flow pump 6 air pump 7 flowmeter 8 aerator 9 backwashing pump 10 reflux pump11 permeate tank

Fig. 1 The schematic of the experimental apparatus



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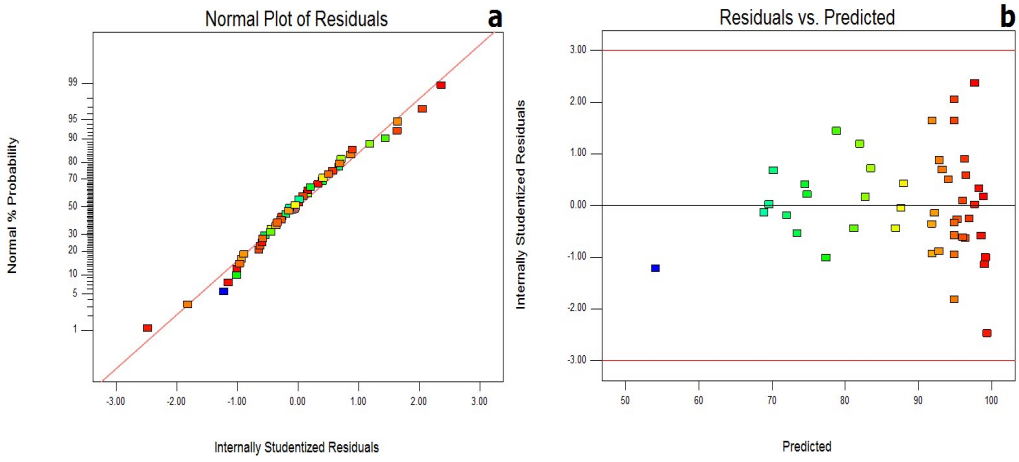

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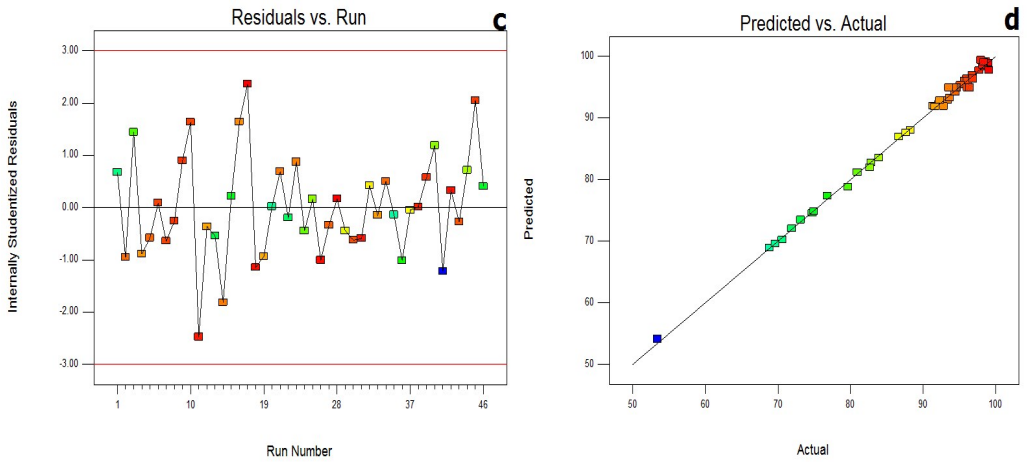

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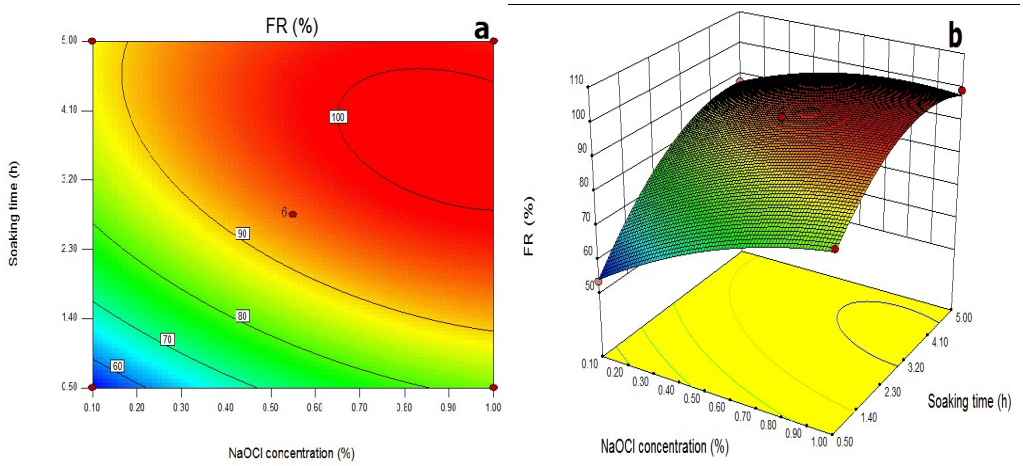

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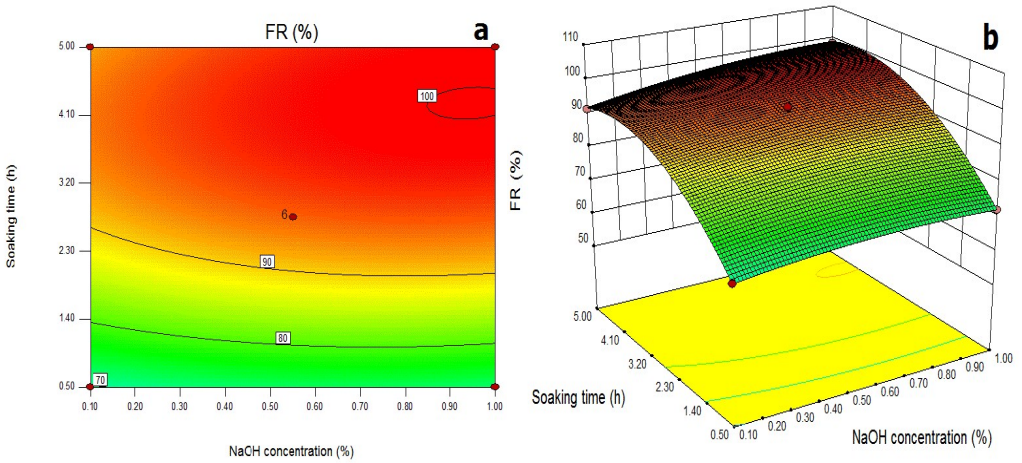

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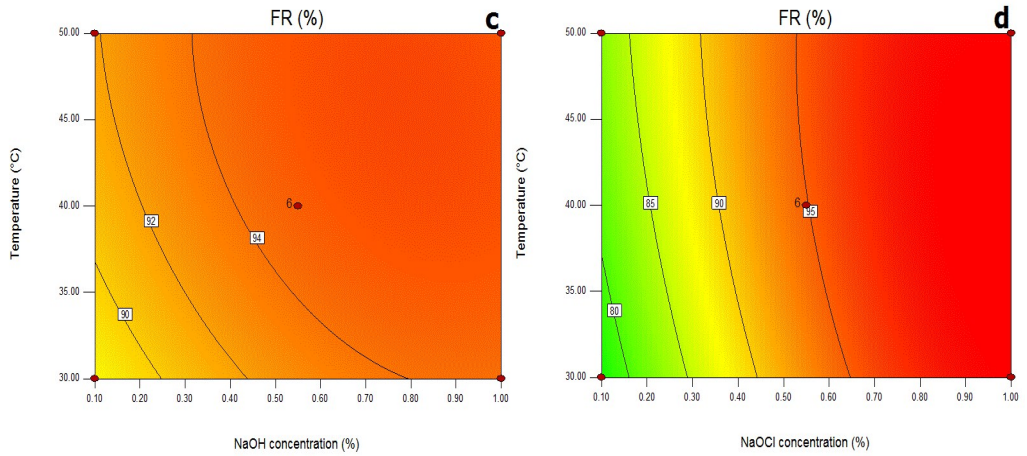

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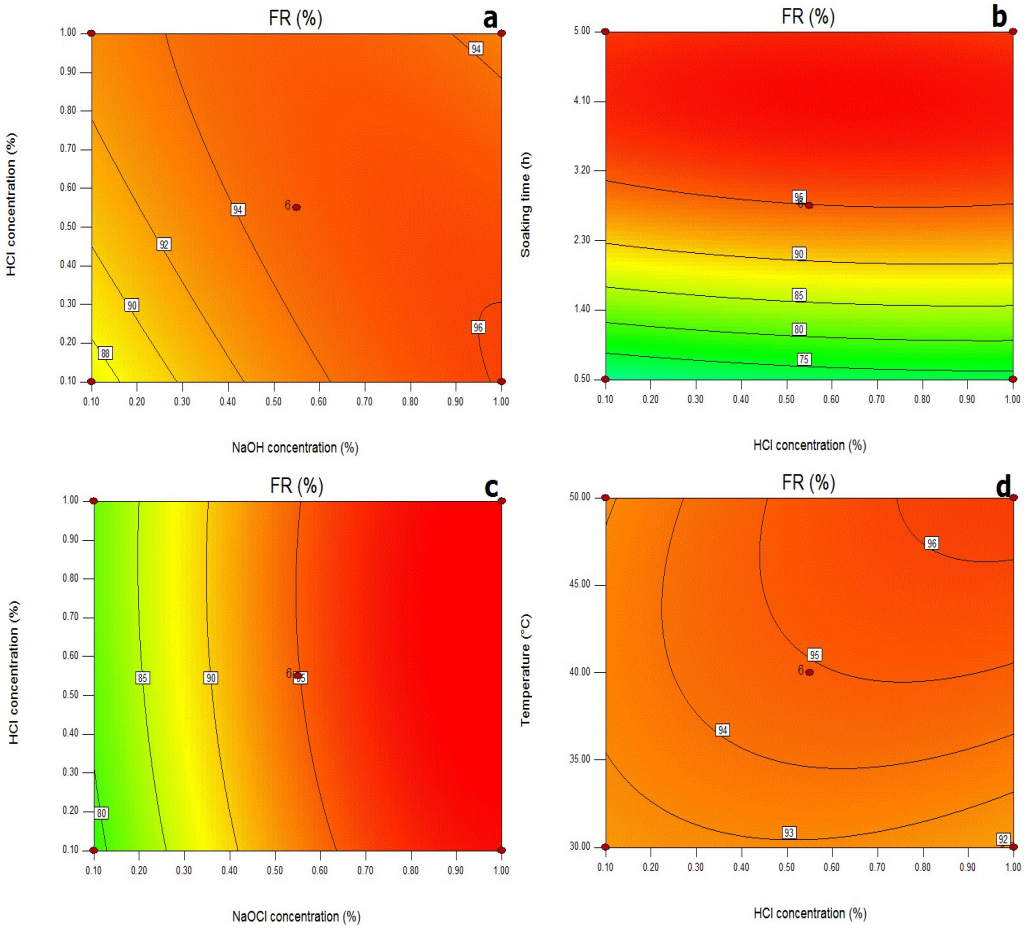

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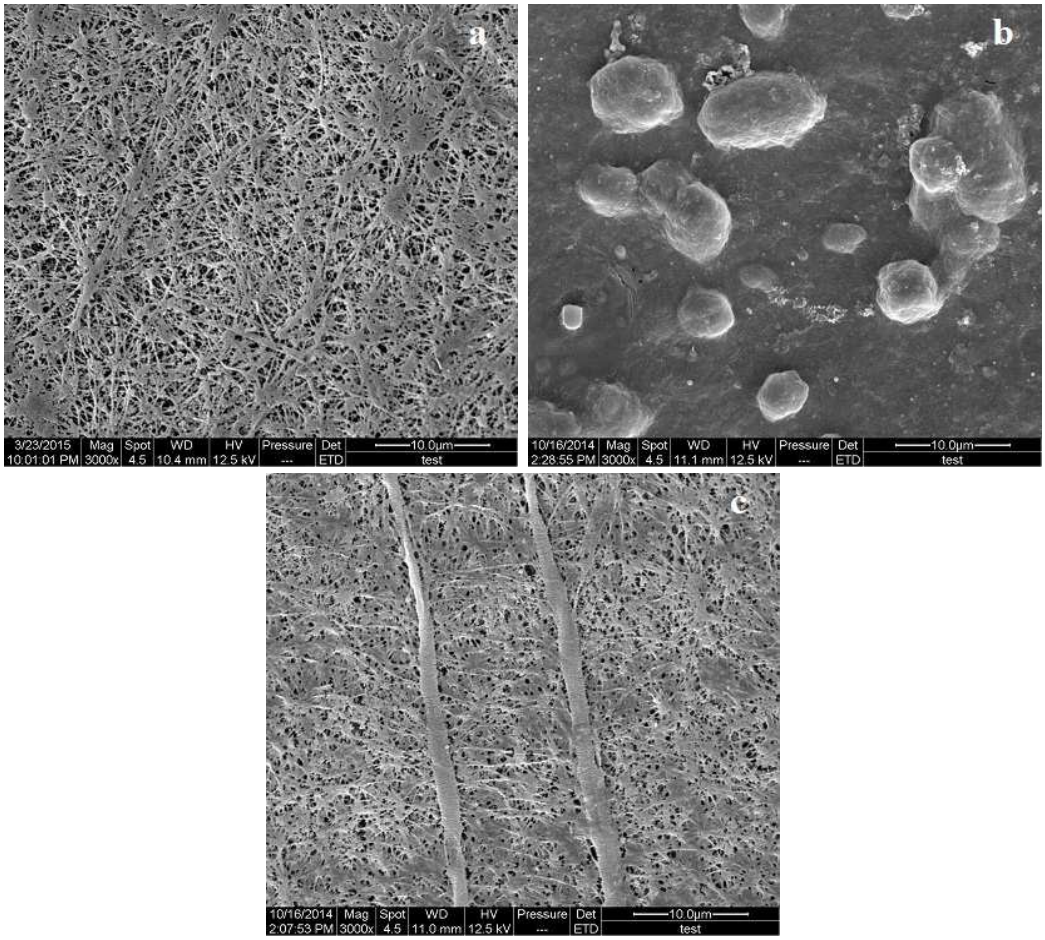

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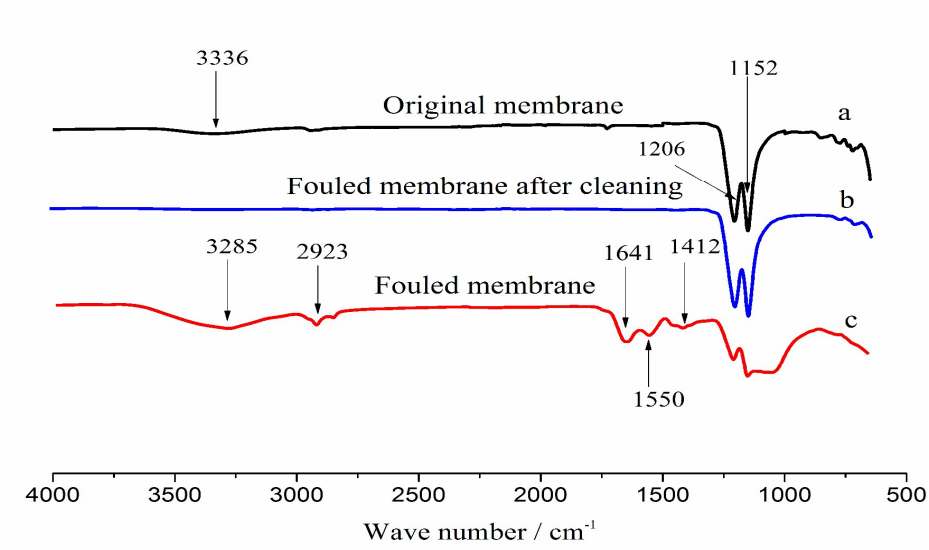

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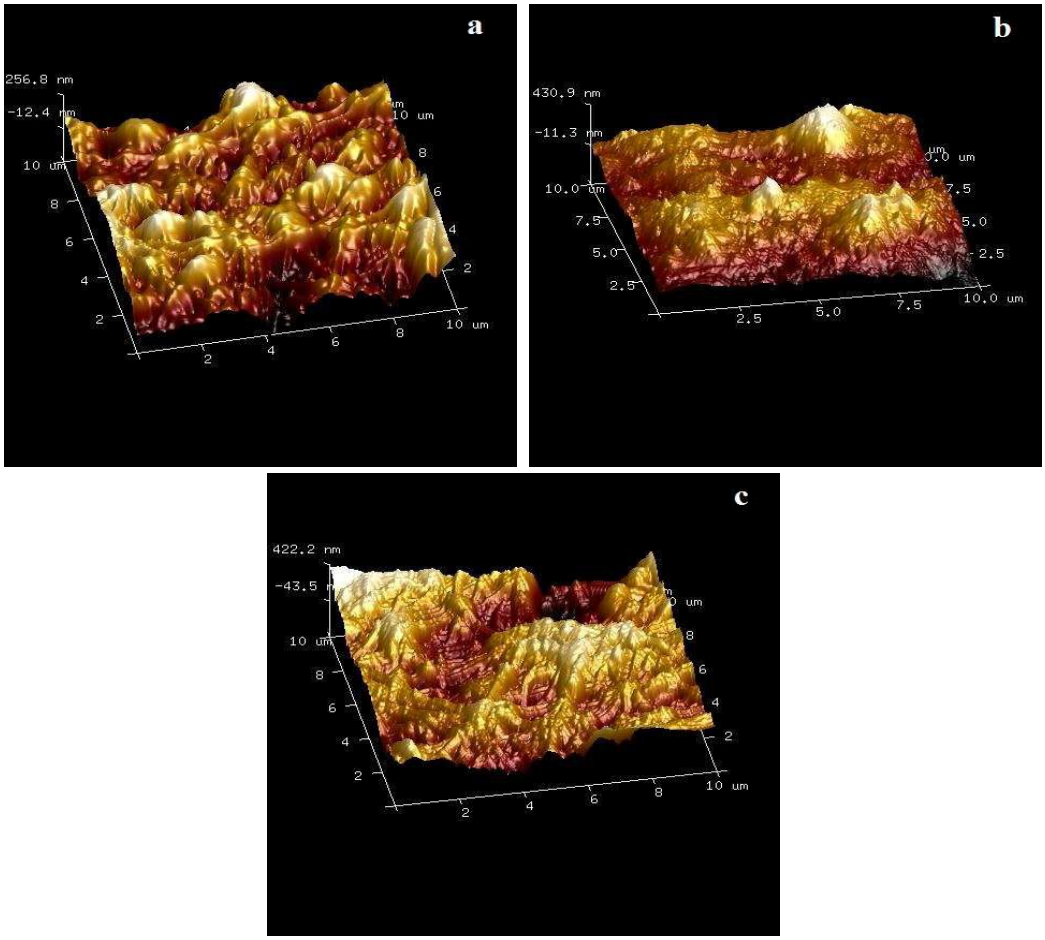

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