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Effect of coagulation pretreatment on microfiltration of paper mill wastewater using electrospun membranes

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ABSTRACT

The pulp and paper mill industry consumes a large amount of water and thus discharges a large amount wastewater, which should be properly treated. Accordingly, this study focused on the application of microfiltration (MF) together with coagulation for the treatment of the paper mill wastewater. A statistical model based on the response surface methodology (RSM) was attempted to determine the optimum coagulation conditions (i.e., coagulant dose, pH, and temperature). Empirical models were developed to understand the interactive correlation between the responses and process variables. After the coagulation, the MF membranes prepared by an electrospinning method were used to treat the wastewater. Nevertheless, it seems that the coagulation conditions optimized for water quality parameters are not always the appropriate conditions for pretreatment of MF feed water.

Keywords: Paper mill wastewater treatment; Coagulation; Microfiltration; Response surface methodology; Electrospun membrane

1. Introduction

The pulp and paper industry is one of the largest industrial sectors in the world, involving the manufacturing companies that convert wood material into a wide variety of pulps, papers and paperboards [1]. By 2025, the production of the global paper industry is expected to grow by over 100%. However, one of the serious issues in the pulp and paper industry is its adverse effect on the water environment, especially due to the production of high strength wastewater [2]. Since the pulp and paper industry uses large amounts of water for pulp preparation, washing, bleaching, and boiler/cooling systems, it produces large volumes of wastewater and residual sludge waste [1,2].

In general, this wastewater is treated for discharge or reuse by processes such as coagulation, sedimentation, membrane filtration, advanced oxidation process, dissolved air floatation (DAF), and activated sludge process [3–5]. Among these processes, membrane filtration holds promise due to its high removal efficiency of various pollutants. Particles and colloids in the wastewater can be removed using microfiltration (MF) or ultrafiltration. If organic matters and dissolved ions should be also eliminated, reverse osmosis can be applied [1].

Among several treatment options, MF has many advantages, including: (1) high quality of product water; (2) small footprint; (3) reduced chemical use; (4) reduced sludge production use; and (5) automatic control of processes [6–8]. Nevertheless, the application of MF for the paper mill wastewater treatment has challenges posed by membrane fouling and subsequent permeability loss. Membrane fouling may be controlled by periodic cleaning and/or enforced pretreatment [6,9]. Coagulation, sedimentation, sand filtration, and DAF have been implemented as a pretreatment process for MF. Among them, coagulation have been the most frequently used not only for water treatment but also for wastewater treatment. The metal cation composed of hydrophobic hydroxide compounds with different charges is used as the coagulant. The coagulant interact with colloidal materials by either charge neutralization or adsorption, leading to coagulation usually followed by sedimentation. The efficiency of

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coagulation treatment is determined by types of coagulants, dose of coagulant, pH, and ionic strength [4,10]. Nevertheless, little information is available on the optimization of coagulation conditions for MF.

In this study, we applied coagulation process as a pretreatment for MF system that is used for paper mill wastewater treatment. A response surface methodology (RSM) was adopted for systematic optimization of the coagulation. RSM is an effective statistical tool to solve multi-variable problems. This technique allows the derivation of the empirical equation for predicting the effectiveness of coagulation process. MF membranes prepared by an electrospinning technique were used to further treat the wastewater after the coagulation. The effect of coagulation pretreatment conditions on MF flux was investigated.

2. Materials and methods

2.1. Raw water

Raw water was sampled from Hansol Artone paper mill in Korea. It was sampled from a water tank mixing the papermaking wastewater and color wastewater. The water quality of this wastewater is listed in Table 1.

2.2. Coagulation

Polyaluminum chloride (PAC as 15% Al_2O_3) was added into the raw water for the pretreatment of MF process. Jar test procedures were performed with the conventional jar apparatus using 1 L wastewater samples. Details in the experimental conditions are provided in Table 2.

Table 1
Water quality of paper mill wastewater as raw water

Parameter	Raw water
pH	6.28
Turbidity, NTU	184
SS, mg/L	340
COD, mg/L	1,920
UVA_{254}, cm^{-1}	0.755
Total alkalinity (as $CaCO_3$), mg/L	608
Conductivity, mS/cm	1.73

Note: COD – chemical oxygen demand; SS – suspended solid; and UVA_{254} – ultraviolet absorption at 254 nm.

Table 2
Operation conditions of coagulation

Parameter	Condition
Volume, L	1
Rapid stirring velocity, rpm	150
Rapid stirring time, min	1
Slow stirring velocity, rpm	40
Slow stirring time, min	10
Sedimentation time, min	30

2.3. Microfiltration

The MF tests were carried out using a flat-sheet module of laboratory-scale equipment. The MF system consists of a feed tank, a membrane module, a peristaltic pump, a flow meter, a pressure meter, an electronic balance, a permeate tank, and a computer. During the operation, the flow rate was frequently checked to guarantee constant pressure condition. Feed tanks for raw water and coagulation tests were used to apply pretreatment to the pulp mill wastewater. The operation conditions of MF are summarized in Table 3.

The membranes used in this study were synthesized through an electrospinning method (Amogreen Tech., Korea). The composing material for the membranes was polyvinylidene fluoride (PVDF), and their nominal pore size was 0.21 μm. Compared with conventional MF membranes, which are prepared by phase inversion methods, the electrospun membranes have higher porosity (>85%). Details on the properties of the membranes are summarized in Table 4.

2.4. Response surface method

RSM is the combination of mathematical and statistical techniques. RSM explored the correlations between independent variables and dependent variables. If the input variable is affecting performance, it is applicable. The purpose of the RSM is to optimize the level of the variables in order to obtain optimal response. The design of experiments such as a central composite design (CCD) and Box–Behnken design may be used to acquire second-degree polynomial models. Then, this model can be used to optimize the conditions for a target variable [11,12]. In this study, a statistical model was applied to analyze the coagulation efficiency. The RSM was used to investigate the influence of process variables such as coagulation conditions (PAC dose, pH, and temperature). The results obtained from the experiments are represented the

Table 3
Operation conditions of MF process

Parameter	Condition
Filtration method	Dead end
Effective membrane area, cm^2	14.25
Pressure, bar	0.4
Temperature, °C	20 ± 5

Table 4
Specifications of electrospun membranes

Parameter	Condition
Material – membrane	PVDF
Material – supporter	PE/PP
Density (g/cm^3)	1.78
Weight (g/cm^2)	42.96
Thickness (μm)	169
Mean pore size (μm)	0.21
Porosity (%)	85.69

relationship between the reaction and independent variables as the multi-order polynomial equation through multiple regression analysis.

2.4.1. Experimental design

In this study, CCD was selected for the optimization of conditions used for coagulation. This method is suitable for fitting a quadratic surface and helps to optimize the effect parameters with the minimum number of experiments, as well as to analyze the interaction between parameters. The CCD was used with three variables and five levels (i.e., –1.414, –1, 0, 1 and 1.414). The PAC dose (X_1), pH (X_2), and temperature (X_3) were selected as the independent variables. The turbidity (Y_1), suspended solid (SS) (Y_2), and chemical oxygen demand (COD) (Y_3) were selected as the responses. Each represents the colloidal, particle concentration, and organic concentration, respectively.

2.4.2. Statistical analysis and regression analysis

Statistical analysis and regression analysis on the experimental results were performed using Minitab 16.2.0 (Minitab, USA). A second-order polynomial model is shown as follows:

$$Y_k = \beta_{k0} + \sum_{i=1}^{3}\beta_{ki}X_i + \sum_{i=1}^{2}\sum_{j=i+1}^{3}\beta_{kij}X_iX_j + \sum_{i=1}^{3}\beta_{kii}X_i^2 \quad (1)$$

where Y_k is the response, namely Y_1 for the turbidity, Y_2 for the SS, Y_3 for the COD, b_{k0} for the constant coefficient, b_{ki} for the linear coefficients, b_{kii} for the quadratic coefficients, b_{kij} for the interaction coefficients, and the coded values of the variables of X_i and X_j. In this work, a second-order polynomial equation was obtained using the uncoded independent variables as follows:

$$Y_k = \beta_{k0} + \beta_{k1}X_1 + \beta_{k2}X_2 + \beta_{k3}X_3 + \beta_{k11}X_1^2 + \beta_{k22}X_2^2 + \beta_{k33}X_3^2 + \beta_{k12}X_1X_2 + \beta_{k13}X_1X_3 + \beta_{k23}X_2X_3 \quad (2)$$

The suitability of the polynomial model was evaluated by R^2.

3. Results and discussion

3.1. Analysis of coagulation treatment efficiency using the response surface method

In this study, the coagulation optimum condition was used to describe the conditions that maximize the rejection of each factor. The experimental design and three resulted responses (Y_1, Y_2, and Y_3) are shown in Table 5. As a result of the RSM, three second-order polynomial regression models were obtained for statistically significant by the analysis of variance (ANOVA). Table 6 summarized that the regression coefficient and p value for Y_1, Y_2, and Y_3. Statistical significance of each resulted coefficient is tested with p value. All the coefficients, which are not significant at $p > 0.05$ level, were removed from the regression equations. The final forms of polynomial models are as follows:

Table 5
CCD and the resultant responses

Standard order	X_1 (PAC dose, mg/L)	X_2 (pH)	X_3 (temperature, °C)	Y_1 (turbidity, NTU)	Y_2 (SS, mg/L)	Y_3 (COD, mg/L)
1	–1 (300)	–1 (4.5)	–1 (25)	131	110	1,617
2	1 (900)	–1 (4.5)	–1 (25)	110	110	1,601
3	–1 (300)	1 (9.5)	–1 (25)	96	190	1,509
4	1 (900)	1 (9.5)	–1 (25)	98.5	180	1,591
5	–1 (300)	–1 (4.5)	1 (55)	120	140	1,627
6	1 (900)	–1 (4.5)	1 (55)	114	130	1,873
7	–1 (300)	1 (9.5)	1 (55)	56	180	1,517
8	1 (900)	1 (9.5)	1 (55)	93.1	170	1,578
9	–1.414 (95.5)	0 (7)	0 (40)	106	180	1,575
10	1.414 (1,104.5)	0 (7)	0 (40)	114	160	1,563
11	0 (600)	–1.414 (2.8)	0 (40)	113	110	1,734
12	0 (600)	1.414 (11.2)	0 (40)	40.6	180	1,363
13	0 (600)	0 (7)	–1.414 (14.8)	130	120	1,730
14	0 (600)	0 (7)	1.414 (65.2)	107	170	1,669
15	0 (600)	0 (7)	0 (40)	96	160	1,555
16	0 (600)	0 (7)	0 (40)	95.2	170	1,557
17	0 (600)	0 (7)	0 (40)	94.5	170	1,564
18	0 (600)	0 (7)	0 (40)	94.8	170	1,567
19	0 (600)	0 (7)	0 (40)	99.6	170	1,553
20	0 (600)	0 (7)	0 (40)	95	160	1,562

$$Y_{1,Turbidity} = 95.844 - 18.537X_2 - 6.669X_3 + 5.045X_1^2 - 6.693X_2^2 + 8.050X_3^2 + 8.325X_1X_2 + 6.2X_1X_3 - 4.8X_2X_3 \quad (3)$$

$$Y_{2,SS} = -166.708 + 25.462X_2 + 8.354X_3 - 7.929X_2^2 - 7.929X_3^2 - 8.750X_2X_3 \quad (4)$$

$$Y_{3,COD} = 1559.48 - 83.98X_2 + 50.63X_3^2 \quad (5)$$

where X_1, X_2, and X_3 take the coded values of the independent variables.

According to the results of ANOVA, Y_1 is dependent on X_1, X_2, and X_3. However, Y_2, and Y_3 seems to depend only on X_2 and X_3. COD and SS are sensitive to pH and temperature than the coagulant dose. All the interaction terms were not included due to low significance. The R^2 for Y_1, Y_2, and Y_3 models were 0.9821, 0.9408, and 0.8261, respectively.

The effects of the independent variables and their interaction on Y_1, Y_2, and Y_3 are illustrated as response surfaces in Figs. 1, 2, and 3, respectively. On the response surface of the effects of two independent variables for Y_k, another variable was at zero level in each plot. Turbidity removal was higher at high temperature and low PAC dose conditions than at low temperature and high PAC dose. However, SS rejection increases as pH decrease. The effect of PAC dose and temperature is negligible. The pH was analyzed as the primary variable in the coagulation process. This result is consistent with those reported by previous studies [3,4,13].

To determine the optimum operating conditions for coagulation, response optimization method was implemented to identify the combination of variable settings that jointly optimize the PAC dose, pH, and temperature. The fitting models in Eqs. (3), (4), and (5) are used to evaluate the impact of multiple variables on a response. The turbidity, SS, and COD were utilized to the minimum as the target value. The results are presented in Fig. 4(a). The combination of the responses (turbidity, SS, and COD) that produces the best results was determined to be PAC dose 557 mg/L, pH 11.2, and temperature 65.2°C. Under this condition, the turbidity, SS, and COD were predicted to be 40 NTU, 155 mg/L, and 1,465 mg/L, respectively. In addition, the coagulation conditions were derived for the removal of colloidal and particulate matter. The turbidity and SS were utilized to the minimum as the target value. The results are shown in Fig. 4(b). The combination of the responses for turbidity and SS that produces

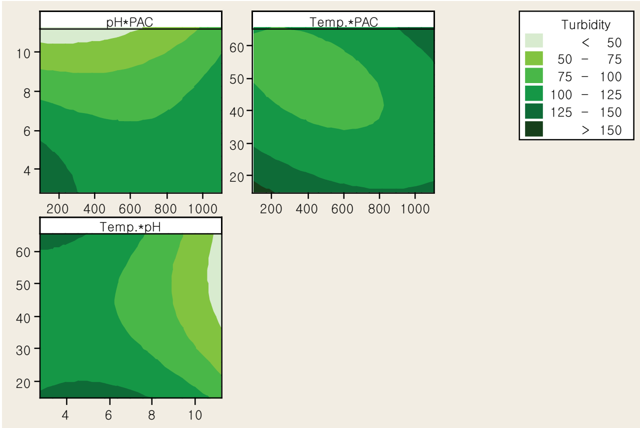

Fig. 1. Response surface of the effects of two independent variables for turbidity, Y_1.

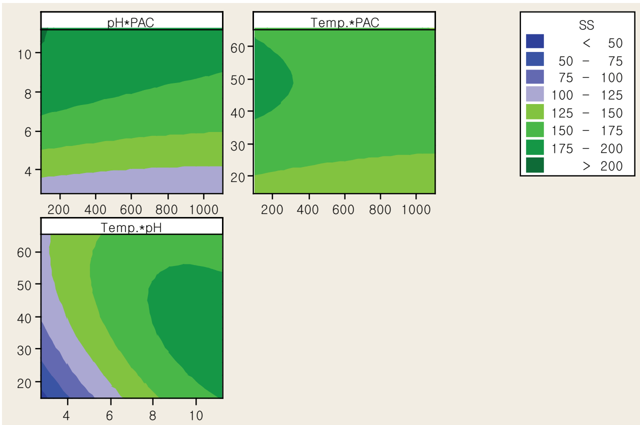

Fig. 2. Response surface of the effects of two independent variables for SS, Y_2.

Table 6
Coefficients of the fitted polynomial model for responses

Parameter	Y_1 (turbidity)		Y_2 (SS)		Y_3 (COD)	
	Coefficient	*p* value	Coefficient	*p* value	Coefficient	*p* value
B_0 (constant)	95.844	<0.0001	166.708	<0.0001	1,559.48	<0.0001
B_1 (X_1, PAC dose)	1.908	0.103	–4.660	0.081	25.83	0.135
B_2 (X_2, pH)	–18.537	<0.0001	25.462	<0.0001	–83.98	<0.0001
B_3 (X_3, temperature)	–6.669	<0.0001	8.354	0.006	12.77	0.441
B_{11}	5.045	0.001	0.910	0.705	4.50	0.777
B_{22}	–6.693	<0.0001	–7.929	0.007	–2.75	0.862
B_{33}	8.050	<0.0001	–7.929	0.007	50.63	0.008
B_{12}	8.325	<0.0001	–1.250	0.698	–10.87	0.612
B_{13}	6.200	0.001	–1.250	0.698	30.13	0.178
B_{23}	–4.800	0.006	–8.750	0.019	–35.88	0.115

the best results was determined to be PAC dose 1,094 mg/L, pH 2.8, and temperature 29°C. Under this condition, the turbidity and SS were predicted to be 98 NTU and 80 mg/L, respectively.

3.2. Effect of coagulation pretreatment on microfiltration

MF experiments were carried out after the optimization of coagulation conditions using RSM. Two optimum conditions were selected to prepare the feed solutions, and the changes in flux with time were examined using these feed solutions. In addition, the untreated wastewater was also used for the comparison of fouling propensity. The pretreatment conditions of the feed solutions in MF are shown in Table 7. Samples 2 and 3 were prepared under the optimum conditions for the removal of turbidity, SS, and COD, and of turbidity and SS, respectively.

Fig. 5 shows the profiles for permeate flux under different pretreatment conditions. The raw wastewater (sample 1) resulted in a rapid flux decline from the beginning. Although the pure water flux was 1,600 L/m^2 h, the initial flux using the feed water was only 50 L/m^2 h, suggesting that the rapid flux decline due to pore blocking occurred. Moreover, the permeate flux after 70 min operation decreased to 13 L/m^2 h, which corresponds to 26% of the initial flux. This is attributed to the structure of the electrospun membrane. Since this membrane has high porosity (>85%), it has a high water flux, leading to accumulation of foulants near the membrane surface. Accordingly, it appears that proper pretreatments are required for this membrane to treat the paper mill wastewater.

As also shown in Fig. 5, the two coagulation conditions determined from Fig. 4 were compared during the MF experiments. When the coagulation was carried out at high temperature and pH condition (sample 2: PAC dose 557 mg/L, pH 11.2, and temperature 65.2°C), the flux was higher than that without pretreatment (raw wastewater). The initial flux was 128 L/m^2 h, and the final flux after 70 min of operation was 23 L/m^2 h, which corresponds to 1.8 times of the flux for raw wastewater. However, when the coagulation was done at low pH condition (sample 3: PAC dose 1,094 mg/L, pH 2.8,

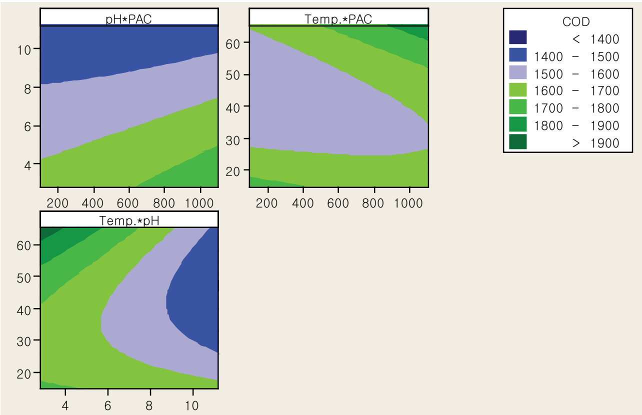

Fig. 3. Response surface of the effects of two independent variables for COD, Y_3.

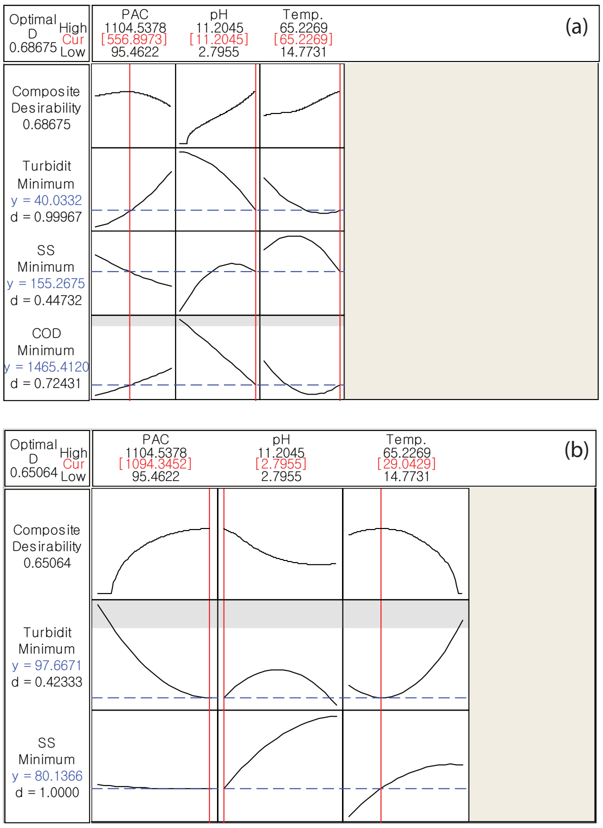

Fig. 4. Optimization of coagulation conditions using response optimization method: (a) the optimal condition for the turbidity, SS, and COD to the minimum and (b) the optimal condition for the turbidity and SS to the minimum.

Table 7
Operation conditions of coagulation as the feed water of MF

	Condition
Sample 1	Without coagulation (raw water)
Sample 2	PAC dose 557 mg/L, pH 11.2, temperature 65.2°C
Sample 3	PAC dose 1,094 mg/L, pH 2.8, temperature 29°C

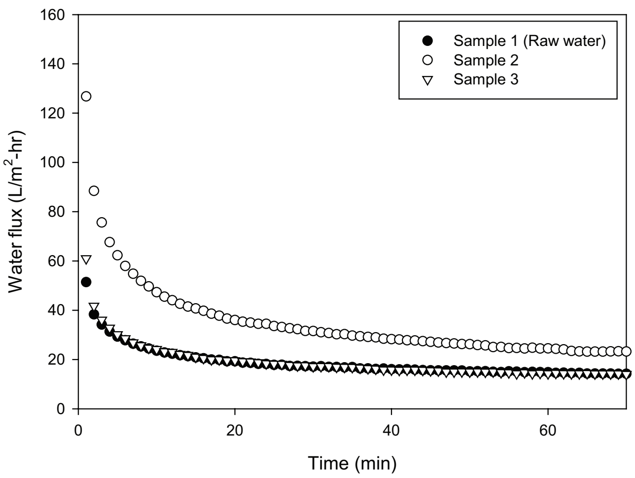

Fig. 5. Effect of coagulation pretreatment on permeate flux in MF.

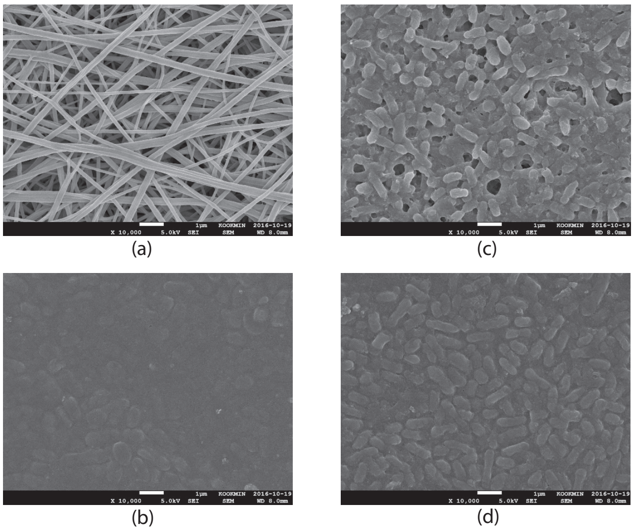

Fig. 6. SEM images for electrospun membranes (magnification: 10,000 times): (a) original membrane; (b) without pretreatment (raw water, sample 1); (c) pretreatment using coagulation at PAC dose 557 mg/L, pH 11.2, and temperature 65.2°C (sample 2); and (d) pretreatment using coagulation at PAC dose 1,094 mg/L, pH 2.8, and temperature 29°C (sample 3).

and temperature 29°C), the flux values were similar to those without pretreatment. This implies that this coagulation condition is not always effective to control fouling.

After the MF experiments, the surfaces of the membranes were examined using the scanning electron microscopy (SEM). As shown in Fig. 6(a), the intact membrane consists of nanofibers with the diameter of approximately 200 nm. Since the membrane was synthesized by electrospinning, its structure is quite different from those by conventional polymeric membranes. The membrane surfaces were covered by cake layer during the MF experiments, as described in Figs. 6(b)–(d). Nevertheless, the amount of cake layer on the membrane surface seems to be different for different feed solutions. The cake layer formed by the sample 2 (PAC dose 557 mg/L, pH 11.2, and temperature 65.2°C) was less dense than those formed by the raw wastewater and sample 3 (PAC dose 1,094 mg/L, pH 2.8, and temperature 29°C). These results match with the trends in the flux profiles in Fig. 5.

4. Conclusions

In this study, the coagulation conditions for the MF of paper mill wastewater were optimized based on RSM. The following conclusions were drawn:

- The removal efficiencies for turbidity, SS, and COD were examined as a function of PAC dose, temperature, and pH. The pH is the most influential variable on the efficiency of coagulation. Turbidity and COD rejection increase as pH and temperature increase; on the other hand, the SS rejection increases as pH decreases. The effect of PAC dose is insignificant.
- The regression equations were obtained by the application of the RSM, allowing the prediction of the coagulation efficiencies. The two optimum conditions were determined using the equations.
- The electrospun membranes were applied to treat the paper mill wastewater. Although the initial flux was very high (~1,600 L/m^2 h), a rapid flux decline was observed from the beginning. This suggests that these membranes cannot be directly applied without any pretreatment.
- Using the wastewater pretreated under these optimum conditions, MF experiments were carried out. The pretreatment was effective when the coagulation was done at high pH and temperature condition (PAC dose 557 mg/L, pH 11.2, and temperature 65.2°C).

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