THE OPTIMIZATION OF FILTERABLENESS OF SUSPENSIONS OBTAINED BY DISSOLVING ULEXITE IN SO_2-SATURATED WATER

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Abstract

In this study, the optimum conditions of cross-flow microfiltration of suspension obtained by dissolving ulexite at 90°C in SO_2-saturated water were determined by Taguchi Method. Experimental parameters were transmembrane pressure, cross-flow rate and membrane porosity. Permeate were measured at 3.8-8.3 $L.min^{-1}$ cross-flow rate and 200-400 kPa transmembrane pressure by using membranes with various pore size. Particle concentration, temperature and pH were taken constant as 22.9 $g.mL^{-1}$, 30°C and 7.33, respectively. As result, optimum conditions were determined 300 kPa for transmembran pressure, 8.3 $L.min^{-1}$ for cross-flow rate using cellulose acetate with 2.5 μm of pore size.

Key words: Optimization, Ulexite, cross-flow filtration, Taguchi Method.

1. Introduction

Microfiltration is a form of filtration that has two common forms. One form is cross-flow separation. In cross-flow separation, a fluid stream runs parallel to a membrane. There is a pressure differential across the membrane. This causes some of the fluid to pass through the membrane, while the remainder continues across the membrane, cleaning it. The other form of filtration is called dead-end filtration or perpendicular filtration. In dead-end filtration, all of the fluid passes through the membrane, and all of the particles that cannot fit through the pores of the membrane are stopped.

Crossflow microfiltration is used in a number of applications, as either a prefiltration step or as a process to separate a fluid from a process stream.

Microfiltration can be defined as the separation of particles of one size from particles of another size in the range of approximately 0.01 µm through 20 µm. The fluid may be either a liquid or a gas.

There have been many investigations on the cross-flow microfiltrasyon [1-7]. In this study, the optimum conditions of cross-flow microfiltration of suspension obtained by dissolving ulexite in SO_2-saturated water were determined by Taguchi Method.

2. Material and Method

Ulexite sample used in the study was supplied from Bigadic in Balikesir, Turkey. The sample was dried in air, crushed with a laboratory mill and ground with a grinder. It was found out by chemical analysis that it contains 35.85% B_2O_3, 15.22% CaO, 6.38% Na_2O, 5.38% MgO, 29.67% H_2O and 7.50 others. X-ray diffractoram of the sample is seen in Figure 1.

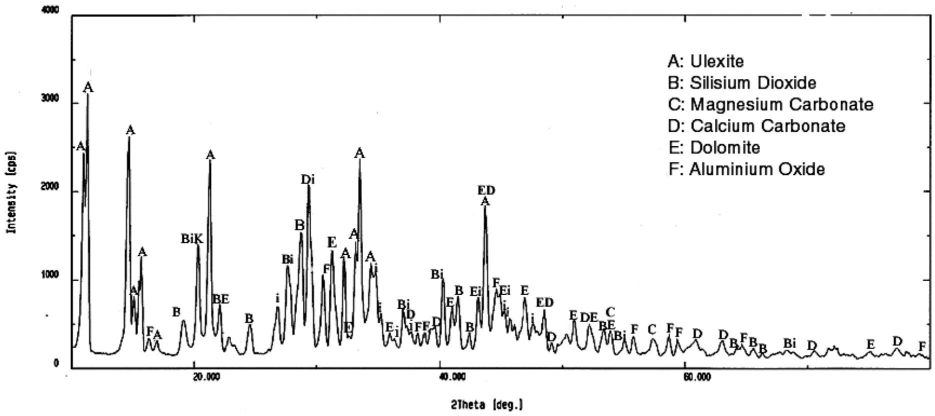

Figure 1. X-Ray difractrogram of the original ulexite mineral.

For the optimization study, impurities in the ground sample firstly were removed by washing with distilled water. And then, 930 g of the washed sample was dissolved in 12 L of SO_2-saturated water at the boiling temperature. Under these conditions, Ca^{2+} and Mg^{2+} ions in the medium were precipitated as $CaSO_3.xH_2O$ and $MgSO_3.yH_2O$. Optimization experiments were carried out for determination of filtration characteristics of the precipitated part by using this suspension. The parameters investigated and their ranges are given in Table 1. X-Ray diffractoram of solid part of suspension used in filtration studies is given in Figure 2.

Table 1. Parameters and their values corresponding to their levels to be studied in experiments

Parameters		Level					
		1	2	3	4	5	6
A	Membran pore size (μm)	0.2 (PTFE)	0.45(PTFE)	1(PTFE)	0.45(Ethyl Acetate)	blue band	black band
B	Crossflow rate ($L.dk^{-1}$)	5,3	6,8	8,3			
C	Transmembran Pressure (kPa)	200	300	400			

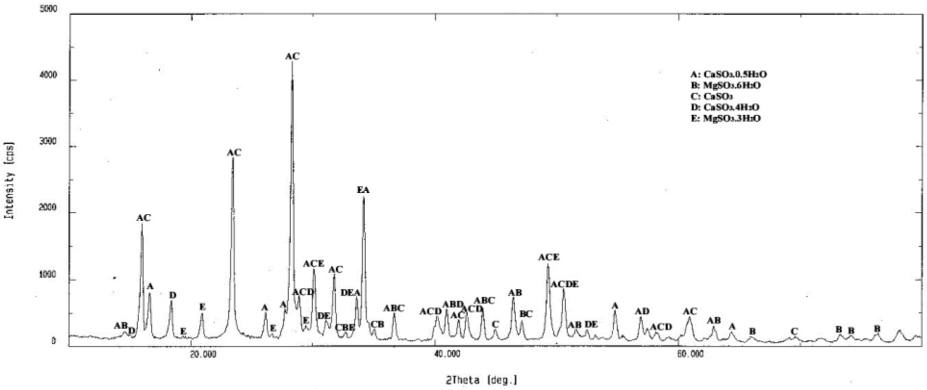

Figure 2. X-Ray diffractogram of solid part used in filtration studies.

Experimental system contains a 20-L feed tank feeding a cross-flow microfiltration unit having 155 cm^2-filtration area and 2 mm-flow cross section. But in studies, this area was make smaller to 9 cm^2 (Figure 3). After suspension prepared as above was added to tank, the tank content was mixed by recycling it during each experiment. Temperature of feed tank was made constant with a cooler. Pressure changes required in system were obtained by keeping inlet and outlet valves at determined positions before. After the conditions were obtained, the recycling valve was turned down according to cross-flow rate which will be obtained and the valve going to system was opened completely. Filtrate from system was transferred to a precision balance and filtrate amounts were recorded with a computer in 15 second during the experiments. Each study lasted 2.5 hours, after the subsequent experimental conditions were set; the system was shutted to change the membrane. Cake and filtrate from system were added to the feed tank again to not change the concentration in it.

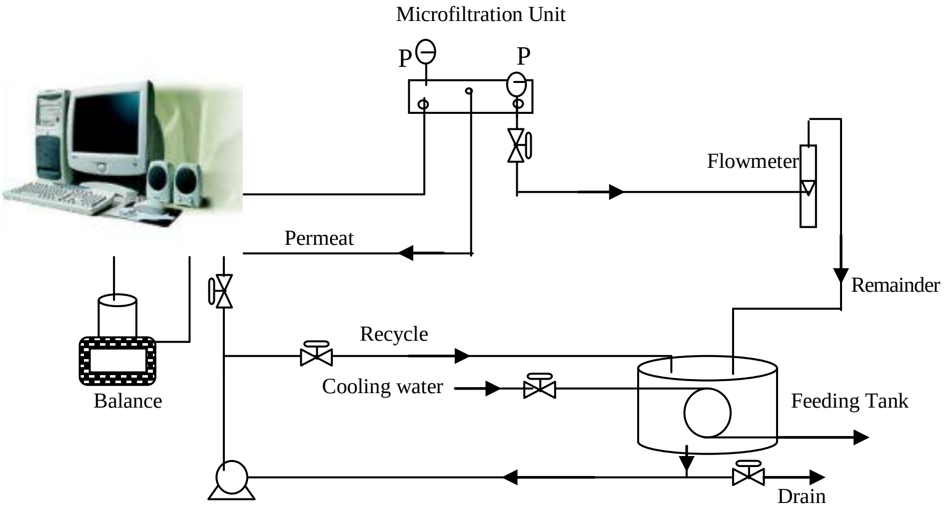

Figure 3. Scheme of the experimental set-up for filtration

To keep the costs at the lowest level, one of the methods based on carrying out the smallest experiments is Taguchi Method improved by Genuchi Taguchi, a Japan scientist. The difference of this method from other statistical experimental design methods is that the parameters affecting an experiment can be investigated in two groups as controllable and non-controllable and many parameters can be examined at more than two levels. Generally, performance characteristics of each product or process must have nominal value or target value.

The aim is to lessen the changeability around this target value. Optimum study conditions which will be determined at the end of experimental study always must give same or close to each other performance values at various study media or various times. For this, the optimization criterion must control to keep the changeability at the minimum level around the performance value. Such an optimization criterion is performance statistics according to Taguchi.

The formulas of performance statistics are the following

Larger-the-better

$$SN_L = -10 Log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \tag{1}$$

Smaller-the-better

$$SN_S = -10 Log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}Y_i^2\right) \tag{2}$$

In Taguchi method, the experiment corresponding to optimum working conditions might not be found in randomized experimental plan table. In such cases; the performance value for optimum conditions can be predicted by using the balanced characteristic of OA. For this purpose; an additive model can be used as follows [8].

$$Y_i = \mu + X_i + e_i \tag{3}$$

If experimental results are in percentage (%), before evaluating Eq 3 Ω transformation of percentage values should be applied first using the Eq. 4 by which values of interest are also later determined by carrying out reverse transformation by using the same equation [9].

$$\Omega(db) = -10 Log\left(\frac{1}{P} - 1\right) \tag{4}$$

Because Eq. 3 is a point estimation, which is calculated by using experimental data in order to determine whether the additive model is adequate or not, the confidence limits for the prediction error must be evaluated [10]. The prediction error is the difference between the observed Y_i and the predicted Y_i. The confidence limits for the prediction error, S_e, is

$$S_e = \pm 2\sqrt{\left[\frac{1}{n_0}\right]\sigma_e^2 + \left[\frac{1}{n_r}\right]\sigma_e^2} \tag{5}$$

$$\sigma_e^2 = \frac{\text{sum of squares due to error}}{\text{degrees of freedom for error}} \tag{6}$$

$$\frac{1}{n_o} = \frac{1}{n} + \left[\frac{1}{n_{A_i}} - \frac{1}{n}\right] + \left[\frac{1}{n_{B_i}} - \frac{1}{n}\right] + \left[\frac{1}{n_{C_i}} - \frac{1}{n}\right] \ldots\ldots \tag{7}$$

If the prediction error is outside these limits, it should be suspected of the possibility that the additive model is not adequate. Otherwise, it can be considered that the additive model to be adequate.

A verification experiment is a powerful tool for detecting the presence of interactions among the control parameters. If the predicted response under the optimum conditions does not match the observed response, then it implies that the interactions are important. If the predicted response matches the observed response, then it implies that the interactions are probably not important and that the additive model is a good approximation [10].

The order of the experiments was obtained by inserting parameters into columns of OA, L_{18} (6^1x3^2), chosen as the experimental plan given in Table 2. But the order of experiments was made random in order to avoid noise sources which had not been considered initially and which could take place during an experiment and affect results in a negative way.

Table 2. $L_{18}\,(6^1\times3^2)$ experimental plan table

Exp. No	Quantities and their levels			Permeate Volume (mL) Experiment(I)	Permeate Volume (mL) Experiment(II)	Average Permeate Volume (mL)	SN Ratio
	A	B	C				
1	1	1	1	1005	978	991.50	59.9234
2	1	2	2	1349	1251	1300.0	62.2604
3	1	3	3	1507	1560	1533.5	63.7098
4	2	1	1	957	948	952.50	59.5770
5	2	2	2	1248	1233	1240.5	61.8715
6	2	3	3	1408	1386	1397.0	62.9031
7	3	1	2	877	912	894.50	59.0266
8	3	2	3	1421	1437	1429.0	63.1002
9	3	3	1	1359	1336	1347.5	62.5896
10	4	1	3	825	844	834.50	58.4268
11	4	2	1	1293	1303	1298.0	62.2653
12	4	3	2	1530	1545	1537.5	63.7360
13	5	1	2	1163	1190	1176.5	61.4101
14	5	2	3	1438	1470	1454.0	63.2497
15	5	3	1	1244	1249	1246.5	61.9138
16	6	1	3	721	762	741.50	57.3923
17	6	2	1	1181	1132	1156.5	61.2571
18	6	3	2	1460	1487	1473.5	63.3659

3. Results and Discussion

3.1. Dissolution reactions during preparation of filtration suspensions:

The following reactions take place during the dissolution process:

$$SO_{2aq)} + H_2O_{(l)} \Leftrightarrow H_2SO_{3(aq)} \quad (8)$$

$$H_2SO_{3(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+ + HSO_3^-{}_{(aq)} \quad (9)$$

$$Na_2O.2CaO.5B_2O_3.16H_2O_{(s)}+6H_3O^+ \rightarrow 2Na^+_{(aq)}+2Ca^{+2}_{(aq)}+10H_3BO_{3(aq)}+10H_2O \quad (10)$$

So, overall reaction is

$$Na_2O.2CaO.5B_2O_3.16H_2O_{(s)} + 2H_2O + 6SO_{2(g)} \rightarrow$$

$$2Na^+_{(aq)} + 2Ca^{+2}_{(aq)} + 6HSO_3^-{}_{(aq)} + 10H_3BO_{3(aq)} \quad 11)$$

When the suspension containing clay minerals obtained by the dissolution of ulexite in SO_2-saturated waters is boiled the following overall reaction carry out

$$2Na^{+}+2Ca^{+2}+6HSO_3^{-}+10H_3BO_3+(2x-18)H_2O \rightarrow 2CaSO_3.xH_2O+2Na^{+}+B_{10}O_{16}^{-2}+4SO_2 \quad (12)$$

Mg^{2+} precipitates as $MgSO_3.yH_2O$, also. So, the obtained suspension contain $CaSO_3.xH_2O$, $MgSO_3.yH_2O$ and clay minerals as solids in addition to Na^+ and $B_4O_7^{2-}$ ions in solution.

3.2. Statistical analysis

The collected data were analyzed by using the MINITAB computer software. In order to see effective parameters and their confidence levels on filtration process, the analysis of variance was performed. A statistical analysis of variance (ANOVA) was performed to see whether process parameters are statistically significant or not. F-test is a tool to see which process parameters have a significant effect on the filtrate volume value. The F value for each process parameter is simply a ratio of mean of the squared deviations to the mean of squared error. Usually, the larger the F value, the greater the effect on the filtrate volume value due to the change of the process parameter. With the performance characteristics and ANOVA analyses, the optimal combination of process parameters can be predicted [11]. The results of variance analysis were given in Table 3.

Table 3. Results of the analysis of variance for the filtration process

Parameters		Degrees of freedom	Sum of squares	Mean of squares	F
A	Membran kind and pore size (μm)	5	108225	21645	1,780
B	Crossflow rate ($L.dk^{-1}$)	2	1592528	796264	65.64
C	Transmembran Pressure (kPa)	2	67644	33822	2.790
	Error	26	315382	12130	
	Total	35	2083779		

To obtain optimal filtration performance,the larger-the-better performance characteristic (Eq.1) has been taken. The order of graphs in Figure 4 is according to the degrees of the influences of parameters on the performance characteristics. The optimal level of a process parameter is the level with the highest SN ratio value calculated by Eq.1.

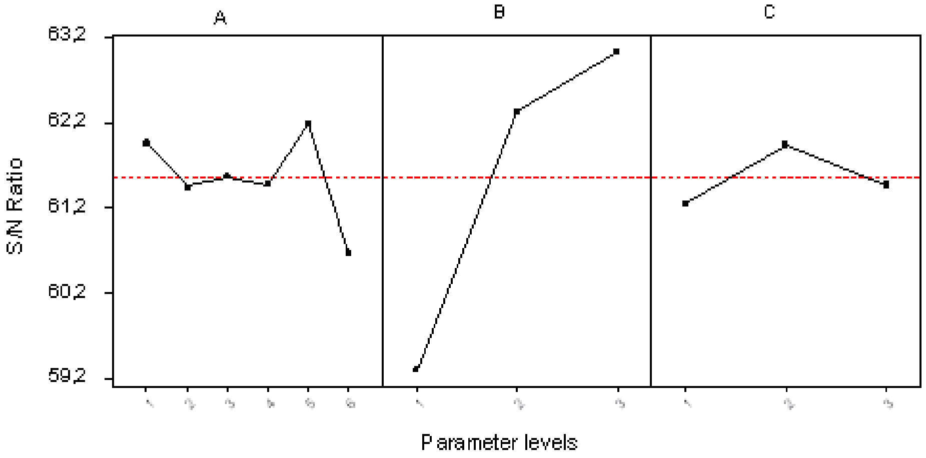

Figure 4. Main effects plot for S/N ratios

If the experimental plan given in Table 2 is studied carefully together with parameter values given as A5 (300 kPa), B3 (8.33 L.min^{-1}) and C2 (2.5 μm cellulose acetate membrane), it can be seen that experiments corresponding to optimum conditions have not been carried out during the experimental work.

In order to test the predicted results, confirmation experiments were carried out twice at the same working conditions. The fact that the filtrate volumes from confirmation experiments are within the calculated confidence intervals calculated from Eqs. 5-7, shows that the experimental results are within ± 5 % in error. This case states that there is a good agreement between the predicted values and experimental values, and the interactive effects of the parameters are indeed negligible. It may be concluded that the additive model is adequate for describing the dependence of this filtration process on the various parameters [10].

4. Conclusions

It is seen in Figure 4 that the parameter levels which SN_L value makes maximum are A_5, B_3 and C_2. So, the parameter levels which filtrate volume makes maximum also, will be A_5, B_3 and C_2. As a result, filterability of suspensions obtained from dissolution of ulexite in SO_2-saturated waters has been analyzed statistically and the conditions which the filterability of the suspension makes maximum have been determinated. Optimum conditions are 300 kPa for transmembran pressure, 8.33 $L.min^{-1}$ for crossflow rate and cellulose acetate membrane with 2.5 µm pore size. Under optimumµ conditions, predicted filtrate volume is 1540 mL and experimental filtrate volume 1572 mL. Predicted value very close to experimental value shows that there is no interaction between the parameters and the model is sufficient to explain the effects of parameters.

Nomenclature

SN_L: performance characteristics for Larger-the-better
SN_S: performance characteristics for Smaller-the-better
Y_i: performance value of ith experiment
µ: the overall mean of performance value
X_i: the fixed effect of the parameter level combination used in ith experiment
e_i : the random error in ith experiment
Ω(db) : the decibel value of percentage value subject to omega transformation
P: the percentage of the product obtained experimentally
S_e: the two-standard-deviation confidence limit
n: the number of rows in the matrix experiment,
n_r: the number of repetition for confirmation experiment or experimental combination
n_{Ai}, n_{Bi}, n_{Ci}, …: the replication number for parameter level Ai, Bi,Ci, …

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