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STATISTICAL EXPERIMENTAL DESIGN OF THE REMOVAL OF DIFFERENT COMPOUNDS FROM SYNTHETIC WASTEWATER BY MICELLAR-ENHANCED ULTRAFILTRATION

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Abstract

In this study, the removal of zinc ions (Zn^{2+}) and n-butanol (n-BuOH), including salt (NaCl) from model synthetic wastewater was investigated by micellar-enhanced ultrafiltration (MEUF) using sodium dodecyl sulfate (SDS). Statistical experimental design was used in order to analyze the effect of initial concentration of Zn^{2+}, n-BuOH, SDS, NaCl on the process performance. Further, the effect of Transmembrane Pressure (TMP) and membrane nominal molecular weight limit (NMWL) were also studied. It was found that n-butanol could not be removed by using MEUF. On the contrary, Zn^{2+} was successfully removed obtaining rejection coefficients up to 99% in the most favorable conditions.

Keywords

MEUF, SDS, Zinc, MODDE, Factorial Design

1. INTRODUCTION

Heavy metal ions such as zinc are detected in the waste streams of mining operations, tanneries, electronics, electroplating and petrochemical industries, as well as in textile mill products [1]. Heavy metals toxicity in air, soil and water is a global problem and a threat to the environment and human health. Therefore, removal of heavy metals is a technological challenge with respect to industrial and environmental applications. Furthermore, volatile organic compounds (VOCs) such as n-butanol are also commonly present in industrial wastewaters. VOCs have been proven to be carcinogens and mutagens [2]. MEUF is a viable membrane-based separation technology for the simultaneous removal of heavy metals and organic compounds [3]. The principle of the process is that the surfactant monomers are aggregated to form micelles at concentrations higher than its critical micelle concentration (CMC) [4]. The solutes can be retained after being trapped by the micelles, whereas the untrapped species readily pass through the UF membranes [5]. Organic compounds are solubilised in the micelle interior and the metal ions get trapped on the surface of the oppositely charged micelles by electrostatic interaction [6]. The advantages of MEUF are low energy consumption as compared to Reverse Osmosis or Nanofiltration, relatively high fluxes and high removal efficiency. There is very few published information on the application of factorial designs by MODDE in the study of MEUF [7]. Factorial design is an efficient technique that can be applied to determine the main effects and interactions of these factors on process performance. Results of factorial design can subsequently be used to optimize and decreases the number of experiments needed. Furthermore, the use of raw material, time and natural resources will be decreased improving the efficiency of the process. This paper reports the removal of zinc ions from aqueous solutions containing n-butanol and sodium chloride by MEUF. The micelles were formed by adding the anionic surfactant sodium dodecyl sulfate (SDS) to the solutions. The main purpose was to separate zinc ions from the aqueous solutions. Additionally, the removal of n-butanol was also expected. Another goal of the present study was to screen the effect of pressure, membrane nominal molecular weight limit, the feed concentration of zinc, n-butanol, sodium chloride and SDS on the process performance.

2. MATERIAL AND METHODS

2.1. Chemicals and equipments

All chemicals involved in the experiments were of analytical reagent grade. Zinc chloride ($ZnCl_2$ extra pure 99.99%) and sodium dodecyl sulfate (SDS, purity > 99%) from Fisher Scientific, UK were used without further purification. SDS has a molecular weight of MW = 288.38 g/mol and it's CMC equal to 8.2mM (2.36 g l^{-1}) [8].

N-butanol (obtained from Kemfine Oy, Finland) was supplied by Aldrich. The distilled water used in this study was purified by a Milli-Q plus water purification system (Millipore, USA) and had an initial resistivity of 18.2 MΩ-cm. N-butanol was determined by gas chromatography with a flame ionized detector (Agilent, 6890N). Sodium chloride (Merk, pro-analysi) was quantified.

The concentration of zinc was determined by Atomic Absorption Spectroscopy (Perkin Elmer 4100 with 3047 and 3044 flame atomization methods). The SDS content was analyzed by Total organic carbon portable analyzer (Sievers 900 Portable).

2.2. Experimental design

A set of experiments was designed by Modde 8.0 (Umetrics) using a fractional factorial design (Table 1). The factors and their respective range to be studied were pressure (P, 20 and 70 psi), SDS feed concentration (C_{SDS}, 3.5 and 20 mM), Zinc feed concentration ($C_{Zn^{2+}}$, 0.5 and 3mM), Sodium Chloride feed concentration (C_{NaCl} 0 and 1w%), butanol feed concentration (C_{BuOH} 1 and 13 mM) and membrane nominal molecular weight limit (NMWL 3 and 10 kDa). Three centre points were included to analyze the reproducibility of the experiments.

Table 1. Experiments conducted using fractional factorial design and their respective results.

Screening Part								
Experimental Number	Factors						Responses	
	C_{SDS} [mM]	C_{BuOH} [mM]	C_{Zn2+} [mM]	C_{NaCl} [mM]	Pres. [psi]	NMWL [kDa]	J [$Lm^{-2}h^{-1}$]	$R_{Zn}2+$ [%]
1	3.5	1	0.5	0	20	3	3.26	73.38
2	20	1	0.5	0	70	3	17.51	99.22
3	3.5	13	0.5	0	70	10	69.51	53.70
4	20	13	0.5	0	20	10	13.15	95.98
5	3.5	1	3	0	70	10	60.81	37.83
6	20	1	3	0	20	10	11.36	96.86
7	3.5	13	3	0	20	3	3.46	36.98
8	20	13	3	0	70	3	20.15	90.02
9	3.5	1	0.5	1	20	10	10.34	17.52
10	20	1	0.5	1	70	10	63.31	57.70
11	3.5	13	0.5	1	70	3	18.60	23.19
12	20	13	0.5	1	20	3	2.64	56.75
13	3.5	1	3	1	70	3	34.10	9.91
14	20	1	3	1	20	3	4.17	42.29
15	3.5	13	3	1	20	10	12.88	13.42
16	20	13	3	1	70	10	54.30	54.87
17	11.75	7	1.75	0.5	45	5	12.21	65.36
18	11.75	7	1.75	0.5	45	5	12.88	65.68
19	11.75	7	1.75	0.5	45	5	12.76	65.05

The measured responses were the rejection coefficients for zinc (R_{Zn}) and butanol (R_{BuOH}) and the absolute permeate flux (J_V), which were calculated with the following equations:

$$R = 1 - \frac{C_p}{C_r}, \quad (1)$$

where C_p and C_r are the zinc or n-butanol concentration in the permeate and retentate, respectively.

$$J_V = \frac{V}{t \times A}, \quad (2)$$

where J_v is the absolute permeate flux, V is the volume of the permeate sample collected, t is the time needed for collecting the permeate sample and A is the membrane effective area. The validity of the empirical models fitted with multiple linear regression (MLR) was tested with analysis of variance (ANOVA). The confidence level used was 95 %.

2.3. Dead-end micellar-enhanced UF experiments

All UF experiments were carried out in batch solvent resistant stirred cell (Millipore, Model 8400) with a capacity of 400 cm^3. In all MEUF tests the TMP was controlled and adjusted with pressurized N_2 gas by means of a transducer. The operating temperature was 25 ± 1°C controlled by an air conditioner. The solution in the reservoir was agitated using a magnetic stirrer to provide efficient mixing at 500 rpm. This stirring speed was selected because it could lead a sufficient agitation to result a homogenic solution without excessive vortex formation. The permeate flux was determined by measuring the first 100 cm^3 (five times 20 cm^3) of the feed solutions. In each experiment the first, second and the fifth permeate sample was analyzed and then integrally averaged because the compositions of the permeate varied during the experiments.

In the dead-end ultrafiltration (UF) experiments, UF flat sheet membranes of Amicon regenerated cellulose (PL series, Millipore) of different nominal molecular weight limits were used. Each membrane has a membrane effective area of 0.004m^2. Only the membranes with a deviation of the pure water flux, measured before and after MEUF tests, smaller than 5 % were repeatedly used. Ultra distilled water was used after each experiment test for membrane cleanings.

2.4. Experimental procedures

The initial feed volume was 200 cm^3. The average permeate flux was calculated by measuring the time needed for collecting permeate samples of 20 cm^3. The ultrafiltration experiments were carried out until 100 cm^3 of the total sample was filtered (VCF = 2). The VCF is defined in Eq. (3):

$$VCF = V_b / V_e \quad (3)$$

where V_b and V_e are the volumes of solutions in the MEUF device at the beginning and at the end of the test, respectively. The membrane was submerged before the concentration tests for 1 h to reach equilibrium with the solution.

3. RESULTS AND DISCUSSIONS

The main purpose was the simultaneous removal of Zn^{2+} and n-BuOH by MEUF. From table 1 can be observed that butanol was not removed using micellar-enhanced ultrafiltration. The reason why the R_{BuOH} is not included in Table 1 is that, in all cases, the rejection coefficients of BuOH were very low (average 5 ± 2 %). Therefore, the research was continued in order to see the effect of the mixture of butanol and salt in the removal of zinc by micellar-enhanced ultrafiltration. In this way, the responses included in the experimental design were R_{Zn} and J_v.

3.1. Effects of factors on the absolute permeate flux

The effect of single factors on the permeate is illustrated in Fig. 1, displaying the change in the response when a factor varies from its low level to its high level while all other factors are kept at their averages. Negligible effects are those where the confidence interval includes zero.

As it can be observed from Fig. 1, pressure has a positive effect on the absolute permeate flux as expected. This means that increasing the pressure, higher permeate flux will be achieved. When pressure is increased the driving force is also increased obtaining a higher flux. NMWL has also a positive effect. Consequently, using a higher pore size membrane higher flux will be observed. Further, concentrations of SDS, BuOH, Zn^{2+} and NaCl show a negligible effect on the absolute permeate flux.

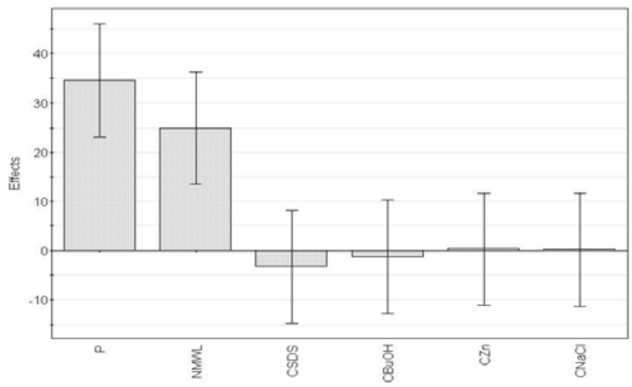

Figure 1. Effect of main factors on the absolute permeate flux

When evaluating the validity of the fitted model with ANOVA, the regression model is statistically significant with a 95% confidence level in the range studied. The response variation percentage explained by the model, R^2, for the permeate flux is 0.85. The response variation percentage predicted by the model, Q^2, is 0.60. The reproducibility of the experiments is good.

3.2. Effect of factors on the rejection coefficient

The effect of single factors on the permeate is illustrated in Fig. 2, displaying the change in the response when a factor varies from its low level to its high level while all other factors are kept at their averages. Negligible effects are those where the confidence interval includes zero.

As it can be observed from Fig. 2, the concentration of SDS, NaCl and the Zn^{2+} have the major effect on the rejection coefficient. Concentration of SDS has a most significant positive effect, thus, when increasing the SDS feed concentration, the rejection coefficient is also increased. This is because at higher SDS concentration, more SDS is present in micellar form. NaCl concentration of the feed has a negative effect on the rejection coefficient, therefore, increasing it will decrease rejection. This result complies with earlier study [9] reported in the literature. Since Na^+ is a monovalent ion, it can readily bind with the negative charge head of the micelle competing with the heavy metal cations. Therefore, rejection coefficient decreases with an increase in the salt concentration. Further, zinc feed concentration also shows a negative effect on the rejection coefficient. Consequently, when increasing the zinc feed concentration rejection coefficient decreases. This shows that MEUF is more efficient for diluted heavy metal streams. Further, concentrations of NMWL, BuOH and pressure show a negligible effect on the rejection coefficient.

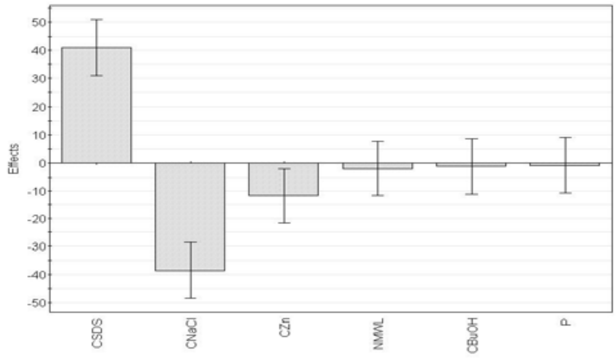

Figure 2. Effect of factors on the rejection coefficient of zinc

When evaluating the validity of the fitted model with ANOVA the regression model is statistically significant with a 95% confidence level in the range studied. The response variation percentage explained by the model, R^2, for the permeate flux is 0.93. The response variation percentage predicted by the model, Q^2, is 0.82. The reproducibility of the experiments is good.

4. CONCLUSIONS

In this study, the removal of zinc ions (Zn^{2+}) and n-butanol (n-BuOH), including salt (NaCl) from model synthetic wastewater was investigated by micellar-enhanced ultrafiltration (MEUF) using an anionic surfactant agent, sodium dodecyl sulfate (SDS).

It was found that n-butanol could not be removed by using MEUF. On the contrary, Zn^{2+} was successfully removed obtaining rejection coefficients up to 99% in the most favorable experimental conditions.

A statistical experimental design (including Screening Part, SP) was used in order to analyze the effect of initial concentration of Zn^{2+}, n-BuOH, SDS, NaCl on the process performance. Further, the effect of Transmembrane Pressure (TMP) and membrane nominal molecular weight limit (NMWL) were also studied.

Pressure and NMWL have the most significant positive effects on the absolute permeate flux. Concentration of SDS has the most important positive effect, while NaCl has the most important negative effect on the rejection coefficient. Further, Zn^{2+} feed concentration has the major negative effect on the rejection coefficient.

By using fractional factorial design, the effects of 6 different factors on the MEUF process performance were evaluated in only 19 experiments. This shows the high effectiveness of experimental design for screening experiments. Further, experimental designs can now be developed as the factors with statistically no significant effect are identified.

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