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A statistical experimental design for the separation of zinc from aqueous solutions containing sodium chloride and *n*-butanol by Micellar-enhanced ultrafiltration

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ABSTRACT

This paper reports the removal of zinc from aqueous solutions containing *n*-butanol and sodium chloride by micellar-enhanced ultrafiltration using the anionic surfactant sodium dodecyl sulfate.

Statistical experimental design was used to analyze the effect of initial concentration of zinc ions, *n*-butanol, sodium dodecyl sulfate and sodium chloride, transmembrane pressure and membrane nominal molecular weight limit on the process performance for screening purposes. The linear models developed for the estimation of the effects of the process parameters were excellent. Pressure and nominal molecular weight limit, and feed concentration of sodium dodecyl sulfate and sodium chloride were the main factors affecting the absolute permeate flux and rejection coefficient towards zinc removal, respectively. Zinc was successfully removed obtaining rejection coefficients up to 99% in the most favorable experimental conditions. On the contrary, no rejection of *n*-butanol was observed.

Keywords: Micellar-enhanced ultrafiltration; Screening fractional factorial design; Zinc; *n*-Butanol; Electrolyte

1. Introduction

The presence of heavy metals (zinc, cadmium, copper, etc) and volatile organic compounds (VOCs) (phenol, dichloromethane, chloroform, n-butanol, etc) in chemical effluents is of major concern due to the threat to the environment and human health. Zinc accumulates in sediments and organisms, from where they may transfer to the food chain. It becomes hazardous reaching certain concentrations producing gastrointestinal distress and diarrhoea [1]. *n*-Butanol contributes to the formation of photochemical smog and produces irritation of eyes, nose and throat in humans [2]. Additionally, chemical effluents can contain salts such as sodium chloride as result of acid-base chemical reaction.

Legislative pressure limiting the discharge of pollutants to aquatic media forces the development and implementation of more efficient technologies. The multicomponent nature of chemical streams provides additional challenges, as possible interactions between components can affect the removal efficiency of the treatment processes.

Currently, the removal of zinc from aqueous solutions is practiced by several physical-chemical processes, such as precipitation, ion exchange, solvent extraction and adsorption. However, most of these techniques are ineffective and economically not feasible [3]. Chemical precipitation treatment generates a large amount of sludge and it leads to additional sludge disposal problems. Furthermore, incomplete removal is achieved at low concentrations of heavy metals. Ion exchange can effectively recover metal ions; however, its disadvantage is the high cost of the resins [4].

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VOCs removal is carried out by activated carbon adsorption and air stripping. However, air stripping only converts a water pollution problem into an air pollution problem [5]. Further, activated carbon adsorption is cost effective only at very low contaminant concentration (<100 µg) [6]. The need for frequent regenerations makes carbon adsorption economically unattractive for high VOC concentration streams.

Micellar-enhanced ultrafiltration (MEUF) is a viable membrane-based separation technology for the removal of heavy metals [7] and organic compounds [8, 9]. The principle of the MEUF process is that the surfactant monomers are aggregated to form micelles at concentrations higher than its critical micelle concentration (CMC) [10]. The solutes are retained after being trapped by the micelles, whereas the untrapped species readily pass through the UF membranes [7]. The main advantages of this method are the simple operation, low energy requirement and high removal efficiency [11]. However, flux decline can limit the performance of MEUF. The permeation of surfactant monomers through the ultrafiltration membrane is another disadvantage.

Traditionally, the study of MEUF performance is conducted using the one variable at a time (OVAT) approach. In OVAT studies, the effect of each experimental factor is investigated altering the level of one factor at a time while maintaining the levels of the other factors constant. The disadvantages of the OVAT approach are the high amount of experiments needed and possibly missing information about the importance of the interaction between factors. The use of statistical experimental design overcomes these limitations. Further, screening designs are used in early stages of an investigation to find the important factors with a small number of experiments and if necessary to modify the ranges. Results of screening may subsequently be used to further optimize 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

Sodium dodecyl sulfate (SDS, purity > 99%) and zinc chloride ($ZnCl_{2,}$ extra pure 99.99%) were obtained from Fisher Scientific, UK, and were used as such without further purification. *n*-Butanol and sodium chloride (pro-analysi) was obtained from Kemfine Oy, Finland and Merck, respectively. Synthetic samples were prepared with deionised water.

2.2. Experimental procedure

The UF experiments were carried out in batch solvent resistant stirred cell (Millipore, Model 8400) with a capacity of 400 cm^3. UF flat sheet membranes of Amicon regenerated cellulose (PL series, Millipore) of different nominal molecular weight limit and membrane effective area of 0.004 m^2 were used. Experiments were conducted at room temperature. The applied overpressure was achieved by nitrogen gas. The initial feed volume was to 200 cm^3. The solution in the feed tank was agitated using a magnetic stirrer to provide an efficient mixing of 500 rpm. The selected stirring speed assured a homogeneous solution without excessive vortex formation. The pH was not adjusted.

Before conducting the UF experiments, the membrane was immersed into the aqueous solution for one hour in order to reach equilibrium. The UF experiments were carried out until 100 cm^3 of the total sample was filtered. The permeate flux was calculated by measuring the time needed for collecting permeate samples of 20 cm^3. The permeate flux varied with time; therefore, logarithmic average was calculated for each UF experiment. The composition of the feed, retentate and permeate were quantified by different methods. Zinc and SDS concentrations were quantified by Atomic Absorption Spectroscopy (Perkin Elmer, AAnalyst 4100) and Total Organic Carbon analyser (Sievers 900), respectively. The amount of *n*-butanol was determined by a gas chromatograph equipped with a flame ionization detector.

Membranes were cleaned after every experiment by rinsing with deionised water for 45 minutes. The membrane washing process was conducted at a pressure of 2.5 bar. Water flux was re-calculated in order to observe the degree of possible membrane damages. Only the membranes with a deviation of the pure water flux, measured before and after the experiments, smaller than 5% were repeatedly used.

2.3. Experimental design

Full factorial design is very useful for the estimation of effects of the factors and their interactions. However, the number of experimental runs required increases rapidly as the number of factors increases. When there are a large number of factors in a factorial design, certain high-order interactions are negligible. Consequently, information on the main effects and low-order interactions may be obtained by running only a fraction of the experiments of the full factorial design i.e., fractional factorial design (FFD) [12].

In this study, a two level FFD with a resolution IV was generated by MODDE 8.0 (Umetrics) for the removal of zinc from aqueous mixtures containing sodium chloride and *n*-butanol. FFD was used to screen out the effect of the main factors and interactions. Resolution IV means that the main effects are not confounded with two factor interactions. Therefore, main effects may be estimated independently. However, two factor interactions are confounded with each other and have not been considered for the development of the linear model (Eq. 1).

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i \tag{1}$$

The factors studied were pressure (*P*), nominal molecular weight limit (*NMWL*), zinc feed concentration ($C_{\mathrm{Zn}^{2+}}$), *n*-butanol feed concentration ($C_{\text{n-BuOH}}$), sodium chloride feed concentration (C_{NaCl}) and SDS feed concentration (C_{SDS}). The levels of the factors are summarized in Table 1. The FFD consisted on 16 experiments (2^{f-2}), where f is the number of factors, and three additional experiments at the center point (Table 2). The former runs were included to analyse the reproducibility of the experiments and the possible curvature of the model.

The measured responses were the rejection coefficient for zinc removal (*R*) and the absolute permeate flux (J_V). *R* was calculated as $R = 1 - C_p/C_r$, where C_p and C_r are the zinc concentration in the permeate and retentate, respectively. J_v was calculated as $J_v = V/(t \times A)$, where *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 goodness the model fitted with multiple linear regression (MLR) was evaluated in terms of coefficient of multiple determination, R^2, adjusted statistic coefficient, R^2_{adj}, and the response variation percentage predicted by the model, Q^2. The validity of the models was also evaluated by the analysis of variance (ANOVA). The confidence level used was 95%.

3. Results and discussions

3.1. Determination of CMC

Physicochemical properties of surfactants changed with the formation of micelles. Thus, physicochemical methods such as electrical conductivity were used for the determination of the CMC of ionic surfactants. When the surfactant concentration was below the CMC value, surfactant monomers behave as strong electrolytes. When the surfactant concentration was above its CMC, the micelles were partially ionised and consequently there was a change in the electrical conductance. Graphically, CMC values were determined as the concentration where an abrupt change of electrical conductivity occurs.

The CMC of SDS was determined by measuring the conductivity of the system (model 20, Denver Instruments). Additionally, the effect of the presence of organic compounds and electrolytes on the CMC of the surfactant was checked (Fig. 1). Changes in CMC could give an insight of the incorporation of a solute in the micelle. The inclusion depended on the structure of the compound. The solubilisation of polar compounds could occur in both outer and inner region of the micelle. Additionally, the incorporation of short chain polar compounds such as ethanol occured on the surface of the micelle. Solubilisation of polar compounds in the inner and on the surface of the micelle produced a slight decrease in the CMC value. On the contrary, molecules solubilised in the outer portion of the micelle were more effective at reducing the CMC. The results showed slight decrease in the CMC value of the surfactant when *n*-butanol was added to the SDS/water system. Consequently, *n*-butanol was solubilised in the inner or on the surface of the micelles. However, McGreevy and Schechter observed

Table 1
Coded and actual levels of the factors for FFD.

Factors	Level		
	Low (–1)	Center (0)	High (+1)
P (psi)	20	45	70
NMWL (kDa)	3	5	10
Zinc feed concentration (mM)	0.5	1.75	3
SDS feed concentration (mM)	3.5	11.75	20
n-Butanol feed concentration (mM)	1	7	13
Sodium chloride feed concentration (wt.%)	0	0.5	1

Table 2
Fractional factorial design and obtained results for the removal of zinc from aqueous mixtures by MEUF.

Run number	Factors						Responses	
	C_{SDS} [mM]	$C_{n\text{-}BuOH}$ [mM]	C_{Zn}^{2+} [mM]	C_{NaCl} [wt%]	Pressure [psi]	NMWL [kDa]	J_V [L m^{-2} h^{-1}]	R [%]
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	70	3	3.46	36.98
8	20	13	3	0	20	3	20.15	90.02
9	3.5	1	0.5	1	70	10	10.34	17.52
10	20	1	0.5	1	70	10	63.31	57.70
11	3.5	13	0.5	1	20	3	18.60	23.19
12	20	13	0.5	1	70	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

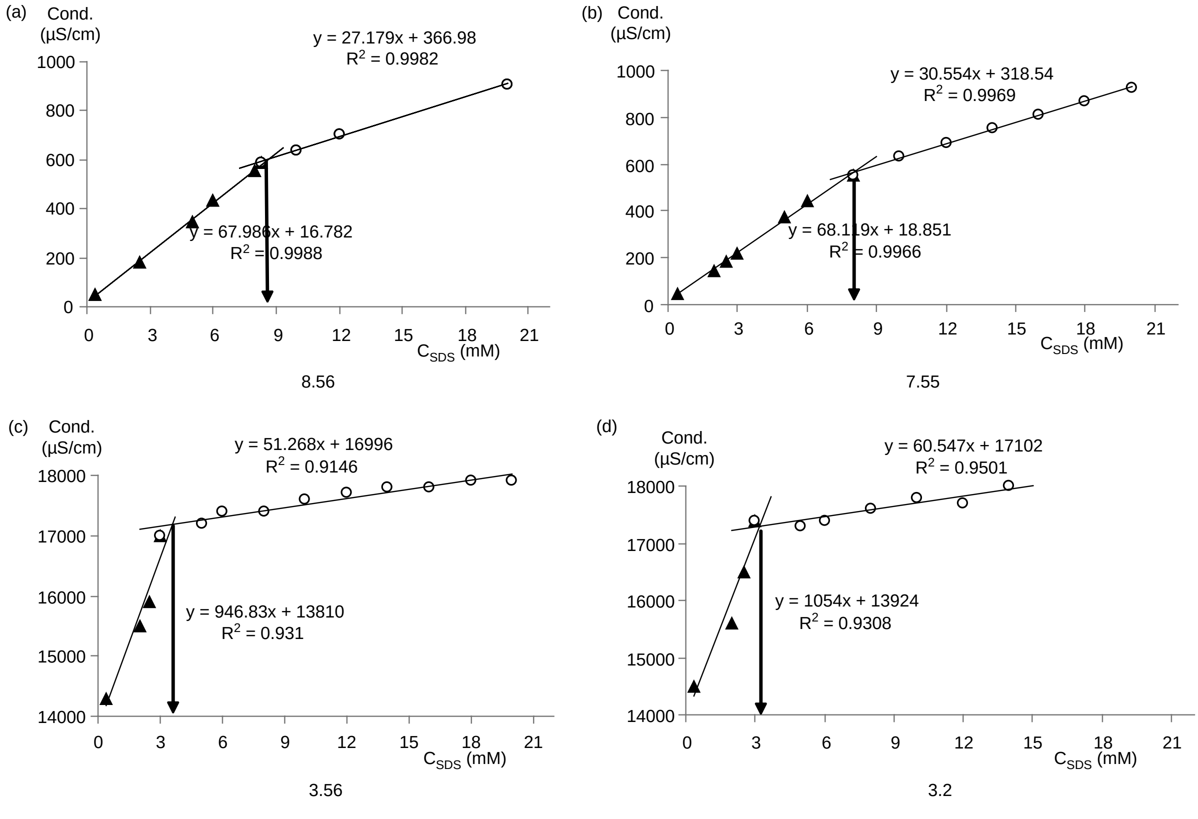

Fig. 1. Determination of CMC by conductivity experiments of the systems (a) SDS/water, (b) SDS/*n*-butanol/water system at constant *n*-butanol concentration of 13 mM, (c) SDS/sodium chloride/water system at constant sodium chloride concentration of 1 wt% and (d) SDS/*n*-butanol/sodium choride/water system at constant *n*-butanol and sodium choride concentration of 13 mM and 1 wt%, respectively.

much stronger diminishment in CMC values when adding similar *n*-butanol feed concentration [13].

Further, Fig. 1 showed that the addition of small amounts of electrolytes decreased strongly the CMC value. The decrease in CMC occurred because the adsorbed compounds (electrolytes and/or organic compounds) decreased the mutual repulsion of the ionic heads of the micelle. Therefore, the work required for micellization and hence, the CMC diminished.

3.2. Removal of zinc from aqueous solutions by MEUF

3.2.1. Data analysis and evaluation of the linear model

Table 2 showed the absolute permeate flux and the rejection coefficients for zinc removal obtained in the UF experiments. As observed rejection coefficients up to 99% was achieved in the removal of zinc. The results were fitted by MLR into linear models with six variables. The models were improved by applying logarithmic transformation to the absolute permeate flux response. Additionally, they were simplified by removing the statistically non-significant terms. However, when the non-significant terms for one response were significant for the other, the term was included in both models. The only term statistically non-significant for both responses, absolute permeate flux and rejection coefficient for zinc removal, was the feed concentration of *n*-butanol.

The adjustment of the model obtained for the absolute permeate flux was excellent, in terms of R^2 (R^2 = 0.977), R^2_{adj} (R^2_{adj} = 0.968) and Q^2 (Q^2 = 0.945). The reproducibility obtained for this response was 99.92%. The model of the rejection coefficient for zinc removal was also well-adjusted. The obtained values of R^2, R^2_{adj}, Q^2 and the reproducibility were 0.942, 0.919, 0.892 and 99.99%, respectively. According to the R^2 values for both models, more than 94% of the data deviation was explained by the two empirical models. A large value of R^2 did not necessarily imply a good regression model as R^2 always increased when adding any variable, significant or not significant, to the model. R^2_{adj}, however, generally increases when significant variables were only added to the model. In our study, R^2 values were in good agreement with R^2_{adj} for both models. Consequently, all the significant terms were included in the empirical models.

Table 3 and 4 showed the ANOVA for the responses absolute permeate flux and the rejection coefficient for zinc removal, respectively. According to the obtained results, $F_{value} > F_{tabulated}$ and $p < 0.05$ for both regression models. This means that the obtained models for absolute permeate flux and the rejection coefficient for zinc removal were both statistically significant with a 95% confidence level in the range studied. Further, the lack of fit for both models was significant with a 95% confidence level ($F_{value} > F_{tabulated}$ and $p < 0.05$) indicating that the model error was significantly larger than the pure error. However, as stated earlier, a very high reproducibility was obtained for the responses, which means that the pure error was artificially close to zero. Therefore the lack of fit was not real. A true lack of fit would have been found if both R^2 and Q^2 values were small.

Further, the need for quadratic terms in the model (existence of curvature) was confirmed by analysing the residual versus variables plot. However this fact did not influence the analysis of the main effects on the responses as the model evaluation was excellent.

3.2.2. Effects of factors on the responses

The effect of single factors on the responses was illustrated in Fig. 2. The figure displayed change in responses when a factor varies from its low level to its high level while all other factors were kept at their averages. Negligible effects were those where the confidence interval includes zero.

As observed in Fig. 2, pressure and NMWL and feed concentration of SDS and sodium chloride were

Table 3
ANOVA for the response absolute permeate flux.

Source of variation	DF	SS	MS	F_{value}	$F_{tabulated}$ ($\alpha = 0.05$)*	Probability (p)	SD
Total corrected	18	3.46	0.19				0.438
Regression	5	3.38	0.68	112.7	3.03	0.000	0.822
Residual	13	0.078	0.006				0.078
Lack of fit (model error)	11	0.078	0.007	46.0	19.41	0.021	0.084
Pure error (replicate error)	2	0.000_3	0.000_2				0.012

*5 % significance level.

[a]DF = degrees of freedom; SS = Sum of squares; MS = Mean square; SD = Standard deviation.

Table 4
ANOVA for the response rejection coefficient for zinc removal.

Source of variation	DF	SS	MS	F_{value}	$F_{tabulated}$ ($\alpha = 0.05$)*	Probability (p)	SD
Total corrected	18	13940	774				27.83
Regression	5	13126	2625	42.0	3.03	0.000	51.24
Residual	13	813	63				7.91
Lack of fit (model error)	11	813	74	745,0	19.41	0.001	8.60
Pure error (replicate error)	2	0.2	0.1				0.32

*5 % significance level.

[a]DF = degrees of freedom; SS = Sum of squares; MS = Mean square; SD = Standard deviation.

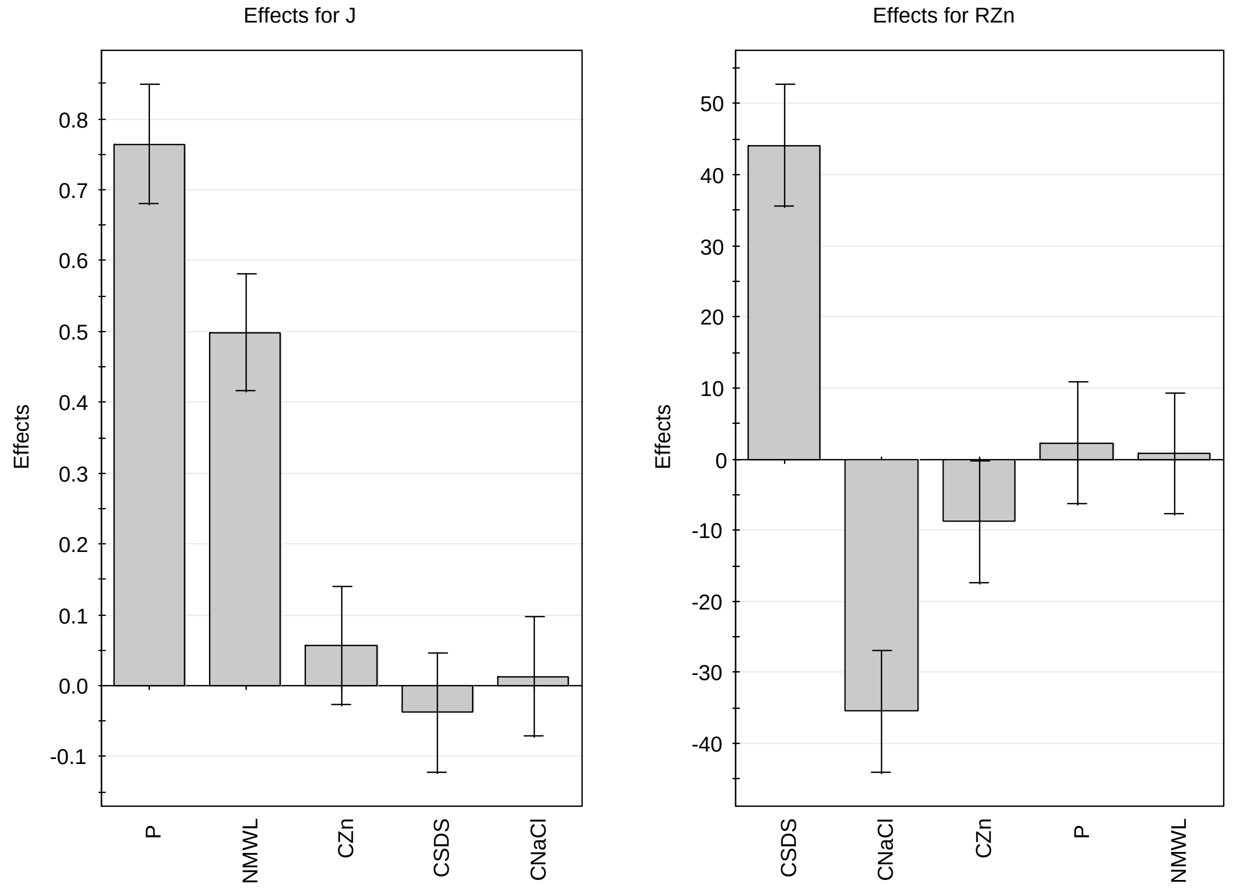

Fig. 2. Effects of the factors on the responses: (a) absolute permeate flux and (b) rejection coefficient for zinc removal.

the main effects affecting the absolute permeate flux and rejection coefficient for zinc removal, respectively. Fig. 2a showed the expected positive effect of pressure on the absolute permeate flux. This means that increasing the pressure higher permeate flux will be achieved. When pressure was increased, the driving force was also increased resulting in higher flux. NMWL had also a positive effect. Consequently, using a higher pore size membrane higher flux was observed. Further, feed concentrations of SDS, zinc and sodium chloride had negligible effect on the absolute permeate flux.

Fig. 2b indicated that NMWL and pressure showed a negligible effect on the rejection coefficient. The feed concentration of SDS had a positive effect on the rejection coefficient for zinc removal. Consequently, when increased the SDS feed concentration, the rejection coefficient also increased. This is because at higher SDS concentration, more SDS was present as micelle instead of being in monomer form. More zinc were trapped by the micelle and retained by the UF membrane, hence obtained higher rejection coefficients. The feed sodium chloride concentration had a negative effect on the rejection coefficient. Therefore, increasing this process factor will decrease the rejection coefficient for zinc removal. This result complies with earlier study [7] reported in the literature. Since Na^+ is a monovalent ion, it can readily bind with the negative charge head of the micelle competing with heavy metal cations. Further, the zinc feed concentration also affected negatively the rejection coefficient. When increasing the zinc feed concentration, the micelles become saturated and higher concentration of surfactant was needed in order to obtain higher rejection coefficients. This indicated that MEUF, contrary to precipitation, was more efficient for the removal of zinc from diluted streams. As the results summarized in Table 2 indicate, up to 99% efficiency for zinc removal was achieved in the most favorable experimental condition. Patterson reported a zinc removal of 93% from general plating waste streams by hydroxide precipitation in similar feed zinc concentration [14]. This would indicate that MEUF can achieve higher removal efficiency.

3.3. Removal of n-butanol from aqueous solutions by MEUF

The results obtained in this study showed that, contrary to our expectations, *n*-butanol was not removed by MEUF in the investigated conditions. This might be because of the presence of electrolytes (sodium chloride and/or zinc chloride) in all the experimental runs.

As stated earlier, a slight decrease of CMC values might have indicated that *n*-butanol was solubilised in the inner part or on the surface (surfactant—water interface) of the micelle. Further, the addition of electrolytes to the solution increased the aggregation number and so also the volume of the micelle. Consequently the solubilisation of the compounds in the inner core was enhanced. As no *n*-butanol rejection was observed in the process, *n*-butanol should be solubilised on the surface of the micelle. Further the lack of rejection might be due to the competition between the electrolytes and the organic compounds.

4. Conclusions

This study showed that zinc was removed by MEUF from solutions containing *n*-butanol and sodium chloride. However, the simultaneous removal of *n*-butanol and zinc are not achieved by MEUF using SDS as surfactant.

MEUF was concluded to be more efficient compared to conventional techniques for the removal of zinc in diluted systems. Further, pressure, NMWL and feed concentration of SDS and sodium chloride were demonstrated to be the main factors affecting the absolute permeate flux and rejection coefficient, respectively.

The evaluation of six factors by nineteen experiments demonstrated the effectiveness of experimental design for screening important factors in early stages of an investigation. The observed curvature of the models describing the responses made complex experimental designs essential for proper modeling and optimization of the removal process. Future work will involve the application of response surface methodology using central composite design.

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