



Micellar-enhanced ultrafiltration for the removal of cadmium and zinc: Use of response surface methodology to improve understanding of process performance and optimisation

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ABSTRACT

In this study, removal of cadmium and zinc from their respective water samples was conducted by micellar-enhanced ultrafiltration (MEUF), using sodium dodecyl sulfate (SDS) as the surfactant. Response surface methodology (RSM) was used for modelling and optimising the process, and to gain a better understanding of the process performance. Face Centred Composite (CCF) Design was used as the experimental design. The factors studied were pressure (P), nominal molecular weight limit (NMWL), heavy metal feed concentration (C_{Zn} , C_{Cd}) and SDS feed concentration (C_{SDS}). Using RSM the retention of heavy metals was maximized while optimising the surfactant to metal ratio (S/M). Response surface plots improved the understanding the effect of the factors on permeate flux. Concentration polarisation was negligible and therefore, high NMWL membranes with high pressure provided high flux with negligible effect on the retention of heavy metals. The optimal conditions of zinc removal were $C_{SDS} = 13.9$ mM, $C_{Zn} = 0.5$ mM, NMWL = 10 kDa and $P = 3.0$ bar, and for cadmium removal $C_{SDS} = 14.2$ mM, $C_{Cd} = 0.5$ mM, NMWL = 10 kDa and $P = 3.0$ bar. The retentions achieved were $98.0 \pm 0.4\%$ for zinc and $99.0 \pm 0.4\%$ for cadmium. To improve resource efficiency, the surfactant was reclaimed after use; 84% of the initial SDS was recovered by precipitation.

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1. Introduction

Heavy metals are of great concern of international environmental legislation because of their extreme toxicity even at low concentration, bioaccumulation and potential food contamination [1]. The Baltic Marine Environmental Commission (Helcom) recommends for chemical industries that the concentration of heavy metals such as cadmium and zinc in wastewater would not exceed the concentration of 0.2 mg/l and 2.0 mg/l, respectively [2].

Traditional techniques for the removal of heavy metals are precipitation, electrodeposition, liquid–liquid extraction, evaporation, adsorption, ion exchange and crystallisation. However, these methods are time consuming, require large amounts of chemi-

cals, involve high operational costs, and often are efficient only at high heavy metal concentration [3–6]. Micellar-enhanced ultrafiltration (MEUF) is an alternative process for the removal of heavy metals, which involves adding an anionic surfactant to the wastewater. The anionic surfactant monomers aggregate and form micelles above the critical micelle concentration (CMC). The heavy metal cations can be mostly trapped in the outer part of the micelles due to electrostatic interaction and thus, they are retained by the ultrafiltration membrane. The untrapped heavy metals and the free surfactant monomers readily pass through the UF membrane [7]. Advantages of MEUF are high removal efficiency, high fluxes and low energy costs [8,9]. On the other hand, anionic surfactants have relatively high CMC [7] and are often expensive; therefore, they constitute a large portion of the operating cost of the process. To improve resource efficiency the surfactant would need to be recovered. Further, flux decline can also affect negatively the efficiency of the membrane separation processes due to concentration polarisation and fouling [10–12], therefore, it is very important to monitor and control it.

Traditionally, the study of MEUF has been conducted using the one variable at a time approach, where the effect of each factor is investigated separately. However, this approach implies a large

Abbreviations: ANOVA, analysis of variance; CCD, Central Composite Design; CCF, Face Centred Composite; MC, critical micelle concentration; MEUF, micellar-enhanced ultrafiltration; MLR, multiple linear regression; NMWL, nominal molecular weight limit; RSM, response surface methodology; SDS, sodium dodecyl sulfate; TOC, total organic carbon.

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Nomenclature

A	membrane effective area (m^2)
b_i	linear coefficient
b_{ii}	quadratic coefficient
b_{ij}	interaction coefficient
b_0	constant coefficient
C_{Cd}	cadmium feed concentration (mM)
C_p	heavy metal concentration in the permeate (mM)
C_r	heavy metal concentration in the retentate (mM)
C_{SDS}	SDS feed concentration (mM)
C_{Zn}	zinc feed concentration (mM)
DF	degrees of freedom
$F_{\text{tabulated}}$	Fisher test critical value
F_{value}	Fisher test calculated value
J_V	permeate flux ($\text{dm}^3/\text{m}^2 \text{ h}$)
K_{sp}	solubility product constant
MS	mean square
N	number of experiments of the design
N_a	number of experiments in two level full factorial design
N_c	number of star points
N_o	number of centred points
p	p -value, probability
P	pressure (bar)
Q^2	response variation percentage predicted by the model
R	retention (%)
R^2	response variation percentage explained by the model
SD	standard deviation
S/M	surfactant to metal concentration ratio
SS	sum of squares
t	time needed for collecting the permeate (h)
V	volume of permeate sample (dm^3)
W	predicted permeate flux ($\text{dm}^3/\text{m}^2 \text{ h}$)
X_i, X_j	factor coded levels
Y	predicted response
Z	predicted retention (%)

amount of experiments and may often miss important conclusions about the effect of (one) experimental variable when the level of another variable is changed (i.e. interaction effects). Further, the process optimisation is inefficient due to the difficulty of finding the true optimum in a reasonable amount of experiments. The use of statistical methods such as response surface methodology (RSM) overcomes the limitations of the one-variable at a time approach. RSM is an efficient statistical tool, which is used for modelling and optimisation of several process variables [13]. Using RSM response surface plots are developed, which give a better understanding of the relationship between the responses and factors. Reported use of response surface methodology in membrane technology is scarce [14–17]. In MEUF, RSM was used only recently for the optimisation of the process conditions in the removal of copper from aqueous solutions [18].

While the MEUF process is widely described in the scientific literature, it requires additional studies to become a mature method for industrial implementation. One of the goals of this study is to establish the applicability of MEUF for removing heavy metals from diluted systems. Previously, a two level full factorial design was used for screening the removal of zinc by MEUF [19]. This work is a continuation of the previous study and aims to model and optimise the removal of zinc and cadmium from their respective water samples by MEUF using RSM approach. The optimisation of the pro-

cess conditions was conducted in order to achieve maximum heavy metal retention with high flux and ensuring good membrane operational stability. Further, the RSM approach was also used to gain an understanding of the concentration polarisation phenomenon as well as the effects of the factors on heavy metal retention and on permeate flux. In addition, the recovery of the anionic surfactant sodium dodecyl sulfate (SDS) has been studied. The ultimate aim of the research, this study is part of, is to develop a methodology using MEUF for industrial wastewater treatment.

2. Materials and methods

2.1. Micellar-enhanced ultrafiltration

The ultrafiltration experiments were carried out in a batch stirred cell (Amicon 8400 stirred cell, Millipore), at room temperature. The stirring speed was maintained constant at 375 rpm to obtain effective agitation and vortex approximately one-third of the depth of the liquid as recommended by the supplier. The pH range of the feed solutions was 5.5–6.3. The applied overpressure was achieved by nitrogen gas. The initial feed volume was 200 cm^3 and the ultrafiltration 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, the logarithmic average was calculated for each UF experiment. Zinc and cadmium concentrations were measured by atomic absorption spectroscopy (PerkinElmer, AAnalyst 4100). SDS concentrations were measured by total organic carbon (TOC) analyser (Sievers 900). Membranes were cleaned afterwards by rinsing with deionised water for 45 min. 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.

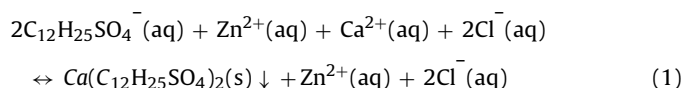
2.2. Materials

For the MEUF experiments sodium dodecyl sulfate (SDS, purity > 99%), zinc chloride (ZnCl_2 , extra pure 99.99%) and cadmium chloride (CdCl_2 , extra pure 99.99%) were obtained from Fisher Scientific, UK, and were used as such without further purification. Samples were prepared using deionised water. UF flat sheet membranes of Amicon regenerated cellulose (PL series, Millipore) of different nominal molecular weight limit and membrane effective area of 0.00418 m^2 were used.

For the recovery of SDS, calcium chloride (CaCl_2 , 98% pure) and sodium carbonate (Na_2CO_3 , 99.5% pure) were purchased from VWR International and J.T. Baker, respectively. Samples were prepared using deionised water.

2.3. Recovery of SDS surfactant

Recovery of SDS was performed from the retentate sample solution of 23 mM surfactant concentration containing zinc. The recovery of the surfactant was performed in two different steps. First, dodecyl sulfate was precipitated as calcium dodecyl sulfate by adding 115 mM CaCl_2 to the retentate sample according to the following reaction,



After the precipitation reaction was completed the centrifugation of the sample was carried out at 10000 rpm for 10 min. The precipitate was separated from the supernatant. The amount of surfactant precipitated was calculated by mass balance and analysing the supernatant using the TOC analyser (Sievers 900). Calcium

dodecyl sulfate is not soluble in water, and it cannot directly be recycled into the MEUF system. Therefore, the precipitated calcium dodecyl sulfate was further treated by adding 22.5 mM Na₂CO₃ solution (stoichiometric amount). Dodecyl sulfate was redissolved as sodium dodecyl sulfate as in the following reaction,



The sodium dodecyl sulfate was collected after centrifugation at 10 000 rpm for 10 min. The supernatant solution containing SDS was analysed by TOC analyser for mass balance calculation.

2.4. Response surface methodology (RSM)

Response surface methodology has 4 major steps, which are experimental design, model fitting, model validation and condition optimisation. Experimental designs such as Central Composite Designs (CCD) are useful for RSM because they do not require an excessive number of experimental runs. In this study, Face Centred Composite Designs (CCF) were generated by MODDE 8.0 (Umetrics) for the investigation of removal of zinc and cadmium, respectively. The designs were based on two-level full factorial design, which were augmented with centre and star points. The total number of experiments of the designs (N) can be calculated as follows,

$$N = N_a + N_o + N_c \quad (3)$$

where N_a is the number of experiments of the two level full factorial design, N_o is the number of centre points and N_c is the number of star points. Further,

$$N_a = 2^n \quad (4)$$

$$N_c = 2 \times n \quad (5)$$

where n is the number of factors studied. The factors studied were pressure (P), nominal molecular weight limit (NMWL), heavy metal feed concentration (C_{Zn} or C_{Cd}) and SDS feed concentration (C_{SDS}). The levels of the factors are summarised in Table 1.

Based on the selected high and low levels of NMWL, the ideal centre point should be 6.5 kDa. In this study, 5 kDa membranes were used as the centre point for NMWL. This fact did not influence considerably in the condition number of the design and the correlation between the factors was negligible, which means that all model coefficients can be estimated independently. In addition, CCD designs are also rotatable, which means that responses can be predicted equally well in all equidistant directions from the centre point. These two desirable properties allow a more accurate calculation of all the model terms (including the quadratic terms) and therefore, more accurate estimation of the shape of the response surface that is being investigated.

Table 2
Scaled and centred coefficients with confidence intervals for the permeate flux when removing zinc and cadmium by MEUF.

Model terms	Permeate flux when removing Zn			Permeate flux when removing Cd		
	Regression coefficients	Confidence interval (\pm)	Probability (p)	Regression coefficients	Confidence interval (\pm)	Probability (p)
Constant	33.87	1.13	0.00 ^a	31.97	2.52	0.00 ^a
X_1	-0.35	0.66	0.28	-0.90	1.37	0.18
X_2	0.068	0.66	0.83	0.10	1.36	0.88
X_3	17.14	0.66	0.00 ^a	13.94	1.37	0.00 ^a
X_4	15.16	0.67	0.00 ^a	16.68	1.37	0.00 ^a
$X_1 \times X_1$	-2.08	1.70	0.02 ^a	-3.40	3.62	0.06
$X_2 \times X_2$	-2.90	1.70	0.00 ^a	-4.45	3.76	0.02 ^a
$X_3 \times X_3$	-0.14	2.27	0.89	9.62	4.46	0.00 ^a
$X_4 \times X_4$	-2.45	1.70	0.01 ^a	-4.03	3.62	0.03 ^a
$X_1 \times X_2$	-0.31	0.71	0.36	0.40	1.45	0.57
$X_3 \times X_4$	9.64	0.70	0.00 ^a	8.15	1.44	0.00 ^a

^a Significant at 5% level ($p < 0.05$).

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

Factors	Level		
	Low (-1)	Centre (0)	High (+1)
Pressure (bar)	1.0	2.0	3.0
NMWL (kDa)	3.0	5.0	10.0
Heavy metal feed concentration (mM)	0.50	1.75	3.0
SDS feed concentration (mM)	8.30	12.45	16.60

The measured responses were the metal retention (R) and the permeate flux (J_V), which were calculated using the following equations:

$$R = 1 - \frac{C_p}{C_r} \quad (6)$$

where C_p and C_r are the heavy metal concentrations in the permeate and retentate, respectively, and

$$J_V = \frac{V}{t \times A} \quad (7)$$

where V is the volume of the permeate sample, t is the time needed for collecting the permeate sample and A is the membrane effective area.

In order to determine the mathematical relationship between the response and factors the following second order polynomial equation was used,

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (8)$$

where Y is the predicted response, b_0 the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and X_i, X_j are the coded levels of process factors studied.

The model was fitted by multiple linear regression (MLR). The validity of the quadratic empirical model was tested with analysis of variance (ANOVA). The confidence level used was 95%.

Optimal conditions according to the models were determined with the help of the MODDE 8.0 software, running the optimiser for each system. The optimiser uses a Nelder Mead simplex method with the fitted response functions to optimise an overall desirability function combining the individual desirability of each response. Optimal conditions were characterised by maximising the retention of the heavy metals.

Table 3
ANOVA table for the permeate flux when removing zinc.

Source of variation	DF ^a	SS ^b	MS ^c	F _{value}	F _{tabulated} (α = 0.05) [*]	Probability (p)	SD ^d
Total corrected	25	10874.4	434.9				20.6
Regression	9	10846.1	1205.1	681.5	2.5	0.00	34.7
Residual	16	28.3	1.8				1.3
Lack of fit	15	21.9	1.5	0.23	245.9	0.95	1.2
Pure error	1	6.4	6.4				2.5

^a DF: degrees of freedom.
^b SS: sum of squares.
^c MS: mean square.
^d SD: standard deviation.
^{*} 5% Significance level.

Table 4
ANOVA table for the permeate flux when removing cadmium.

Source of variation	DF ^a	SS ^b	MS ^c	F _{value}	F _{tabulated} (α = 0.05) [*]	Probability (p)	SD ^d
Total corrected	26	9986.9	384.1				19.6
Regression	10	9867.2	986.7	131.9	2.5	0.00	31.4
Residual	16	119.5	7.5				2.7
Lack of fit	14	117.8	8.4	8.7	19.4	0.11	2.9
Pure error	2	1.9	0.97				0.98

^a DF: degrees of freedom.
^b SS: sum of squares.
^c MS: mean square.
^d SD: standard deviation.
^{*} 5% Significance level.

3. Results and discussion

Appendices A and B show the detailed experimental design with coded factor levels and the responses observed for zinc and cadmium, respectively.

3.1. Permeate flux

3.1.1. Empirical models for permeate flux

Table 2 shows the regression (MLR) coefficients with confidence intervals for the permeate flux when removing zinc and cadmium. The coefficients represent the change in the response when a factor varies from 0 to +1 in coded unit, while the other factors are kept at their averages. The coefficients refer to the data scaled and centred and they are significant at the used confidence level when p < 0.05.

Considering only the statistically significant coefficients the following models with coded values for the permeate flux (W) of zinc and cadmium were developed,

$$W_{Zn} = 33.87 + 17.14X_3 + 15.16X_4 - 2.08X_1^2 - 2.90X_2^2 - 2.45X_4^2 + 9.64X_3X_4 \tag{9}$$

$$W_{Cd} = 31.97 + 13.94X_3 + 16.68X_4 - 4.45X_2^2 + 9.62X_3^2 - 4.03X_4^2 + 8.15X_3X_4 \tag{10}$$

As it can be observed from Eqs. (9) and (10) the empirical models for zinc and cadmium are very similar. The coefficient terms

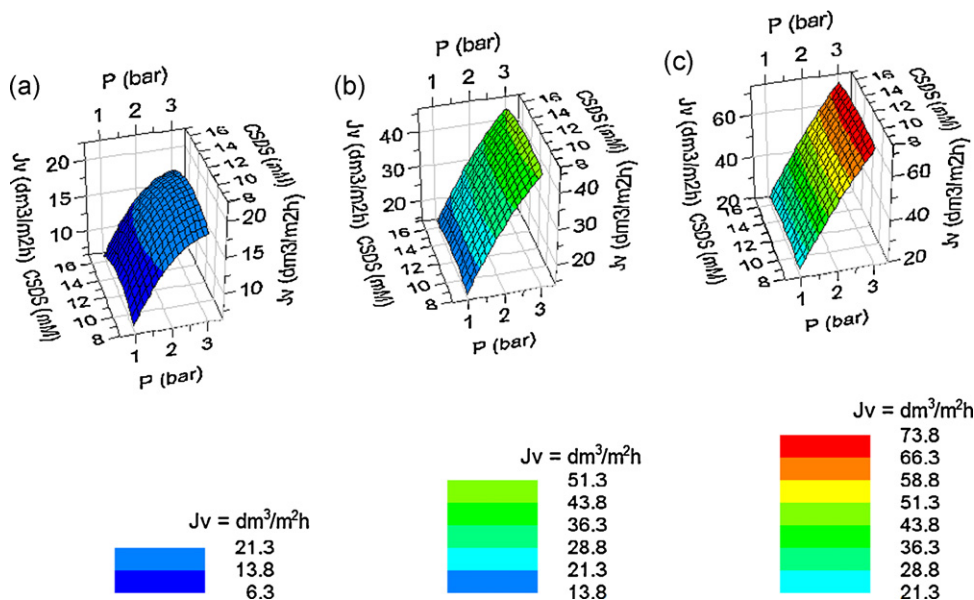


Fig. 1. Predicted permeate flux values for the removal of zinc, spanned by the pressure (P) and SDS feed concentration (C_{SDS}) for three different level of NMWL (a) 3 kDa, (b) 5 kDa and (c) 10 kDa. The zinc feed concentration (C_{Zn}) is 1.75 mM.

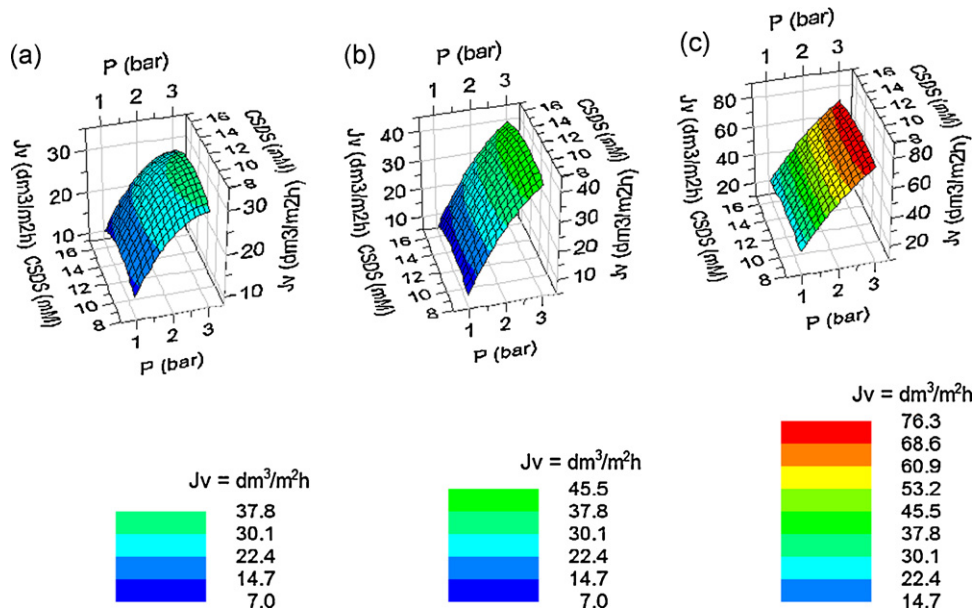


Fig. 2. Predicted permeate flux values for the removal of cadmium, spanned by the pressure (P) and SDS feed concentration (C_{SDS}) for three different level of NMWL (a) 3 kDa, (b) 5 kDa and (c) 10 kDa. The cadmium feed concentration (C_{Cd}) is 1.75 mM.

included in the models are not exact numbers, but terms which contains uncertainty due to the experimental errors.

When evaluating the validity of the fitted models for zinc and cadmium with ANOVA (Tables 3 and 4), results show that $F_{\text{value}} > F_{\text{tabulated}}$ and $p < 0.05$. Therefore, the regression models are statistically significant with the 95% confidence level in the range studied. In addition, the lack of fit is not significant in neither of the developed models with the 95% confidence level ($p > 0.05$).

In the removal of zinc the response variation percentage explained by the model, R^2 , is 0.997. The adjusted statistical coefficient, R^2_{adj} , is 0.996. Further, the response variation percentage predicted by the model, Q^2 , is 0.993. In the case of cadmium removal R^2 , R^2_{adj} and Q^2 are 0.988, 0.981 and 0.960, respectively. These results are very satisfactory and show the good validity of the models developed.

3.1.2. The effects of factors on the permeate flux

From the empirical models described in Section 3.1.1 response surface plots were developed, which can be used to understand the effect of the factors on the permeate flux. Further, the response surface plots were also developed to investigate the concentration polarisation phenomenon and the effect of the factors on it.

3.1.2.1. Effect of pressure and NMWL. Figs. 1 and 2 shows the predicted permeate flux values, spanned by pressure and SDS feed concentration for three different levels of NMWL. As it can be observed, pressure has a positive effect on the permeate flux. When increasing the pressure the driving force is also increased and, therefore, the flux is higher. A linear increase in permeate flux with pressure indicates that the separation process is under the pressure controlled region, where the concentration polarisation is negligible. This is observed for the 5 kDa and 10 kDa membranes. However, in the case of the 3 kDa membrane a slight curvature is observed achieving a plateau when the pressure is around 3 bar. Concentration polarisation is caused by the accumulation of retained solutes, i.e. micelles, on the membrane surface where their concentration will gradually increase. The micelles retained on the membrane surface generate a deposited layer on the membrane surface increasing the resistance against the solvent transmembrane flux. When concentration polarisation is more severe, increasing the pressure the deposited micelles layer is compressed and the flux-pressure relationship becomes non-linear [8]. The deviation from linearity of the pressure-flux relationship shows the occurrence of concentration polarisation phenomenon on the 3 kDa membrane. However, the relative flux values through the 3 kDa membrane were close to 0.8 (data not shown) therefore, the flux decline was about 20%. The flux decline observed

Table 5
Scaled and centred coefficients with confidence intervals for the retention of zinc and cadmium.

Model terms	Zn retention			Cd retention		
	Regression coefficients	Confidence interval (\pm)	Probability (p)	Regression coefficients	Confidence interval (\pm)	Probability (p)
Constant	97.68	0.85	0.00 ^a	97.09	0.33	0.00 ^a
X_1	3.43	0.50	0.00 ^a	3.53	0.18	0.00 ^a
X_2	-2.49	0.50	0.00 ^a	-2.60	0.18	0.00 ^a
X_3	0.013	0.49	0.96	-0.17	0.18	0.06
X_4	0.12	0.50	0.62	0.20	0.18	0.03 ^a
$X_1 \times X_1$	-2.01	1.28	0.00 ^a	-1.62	0.47	0.00 ^a
$X_2 \times X_2$	-0.76	1.28	0.23	-0.30	0.49	0.22
$X_3 \times X_3$	-0.46	1.69	0.57	-0.40	0.59	0.17
$X_4 \times X_4$	-0.31	1.28	0.61	-0.33	0.47	0.16
$X_1 \times X_2$	2.02	0.53	0.00 ^a	2.19	0.19	0.00 ^a
$X_3 \times X_4$	0.07	0.53	0.80	0.38	0.19	0.00 ^a

^a Significant at 5% level ($p < 0.05$).

Table 6
ANOVA table for zinc retention.

Source of variation	DF ^a	SS ^b	MS ^c	F _{value}	F _{tabulated} ($\alpha = 0.05$) [*]	Probability (p)	SD ^d
Total corrected	25	447.7	17.9				4.2
Regression	9	431.7	48.0	47.8	2.5	0.00	6.9
Residual	16	16.1	1.0				1.0
Lack of fit	15	12.3	0.82	0.22	246.0	0.95	0.90
Pure error	1	3.8	3.8				1.9

^a DF: degrees of freedom.^b SS: sum of squares.^c MS: mean square.^d SD: standard deviation.^{*} 5% Significance level.

is not significant showing that concentration polarisation was not severe.

3.1.2.2. Effect of surfactant feed concentration. In Figs. 1 and 2 the negligible effect of the SDS feed concentration on the permeate flux can be observed. The decrease in permeate flux due to the increase in the surfactant feed concentration has before been reported [8,9]. At a high surfactant feed concentration, the surfactant concentration in the retentate is also high and, therefore, concentration polarisation phenomenon is enhanced [8,9]. However, Scamehorn et al. [20] reported that as long as the retentate SDS concentration does not exceed the concentration of 200–300 mM, the concentration polarisation effect is not severe. In this study, the SDS retentate concentration range obtained varied from 13 mM at the SDS initial feed concentration of 8.3 mM, to 33 mM at the SDS initial feed concentration of 16.6 mM. Undoubtedly, this retentate concentration range is substantially below the level, which would cause a considerable flux decline. Other studies also reported [21,22] that the flux decline due to the increase in SDS surfactant concentration is enhanced for membranes with higher cut-off values and more hydrophobic properties. In this study, the interaction between NMWL and C_{SDS} was not significant. This might be due to the hydrophilic character of the membranes used. Regenerated cellulose membranes are hydrophilic membranes where adsorption of the surfactant on the membrane surface might not be enhanced. It can be asserted that all the membranes used in this study showed good operational stability.

3.1.2.3. Effect of heavy metal feed concentration. Few authors studied the effect of the heavy metal feed concentration on the permeate flux [23,24]. Das et al. [23] observed a significant decline in permeate flux when increasing the concentration of divalent metal counter ions at fixed feed surfactant concentration. They reported that in the presence of metal ions, positively charged metal ions bridge more than one negatively charged micelles leading to a formation of gel layer on the membrane surface at lower concentration of surfactants. Further, the increase in cation concentration such as heavy metal cations releases the repulsive forces between the head groups, and the formation of micelles become easier [25], i.e.

the CMC decreases. When decreasing the CMC of the surfactant, more surfactant monomers will be in micellar form and, therefore, the surfactant concentration in the retentate will be increased enhancing the flux decline [26]. In this study, the metal feed concentration showed a negligible effect on the permeate flux. At fixed feed SDS concentration of 16.6 mM, the surfactant concentration in the retentate increased only by 3% when increasing the metal feed concentration from 0.5 mM to 3 mM. This increase in SDS retentate concentration is not significant and, consequently no flux decline was observed due to metal feed concentration.

3.2. Heavy metal retention

3.2.1. Empirical models for heavy metal retention

Table 5 shows the scaled and centred coefficients with the confidence intervals for the retention of zinc and cadmium, respectively. Considering only the statistically significant coefficients, the following models with coded values for the rejection coefficient (Z) of zinc and cadmium were developed,

$$Z_{Zn} = 97.68 + 3.43X_1 - 2.49X_2 - 2.01X_1^2 + 2.02X_1X_2 \quad (11)$$

$$Z_{Cd} = 97.09 + 3.53X_1 - 2.60X_2 + 0.20X_4 - 1.62X_1^2 + 2.19X_1X_2 + 0.38X_3X_4 \quad (12)$$

The empirical models (Eqs. (11) and (12)) for divalent zinc and cadmium are very similar. This might be because the metal valence is the dominant characteristic determining the separation efficiency in MEUF when removing multivalent inorganic metal ions from water [20].

When evaluating the validity of the fitted models for zinc and cadmium with ANOVA (Tables 6 and 7), results show that $F_{value} > F_{tabulated}$ and $p < 0.05$. Therefore, the regression models are statistically significant with the 95% confidence level in the range studied. In addition, the lack of fit is not significant in either of the developed models with the 95% confidence level ($p > 0.05$).

In the removal of zinc the response variation percentage explained by the model, R^2 , is 0.964. The adjusted statistic coefficient, R^2_{adj} , is 0.944. Further, the response variation percentage

Table 7
ANOVA table for cadmium retention.

Source of variation	DF ^a	SS ^b	MS ^c	F _{value}	F _{tabulated} ($\alpha = 0.05$) [*]	Probability (p)	SD ^d
Total corrected	26	463.3	17.8				4.2
Regression	10	461.2	46.1	359.9	2.5	0.00	6.8
Residual	16	2.1	0.1				0.36
Lack of fit	14	2.0	0.2	16.3	19.4	0.06	0.38
Pure error	2	0.02	0.01				0.09

^a DF: degrees of freedom.^b SS: sum of squares.^c MS: mean square.^d SD: standard deviation.^{*} 5% Significance level.

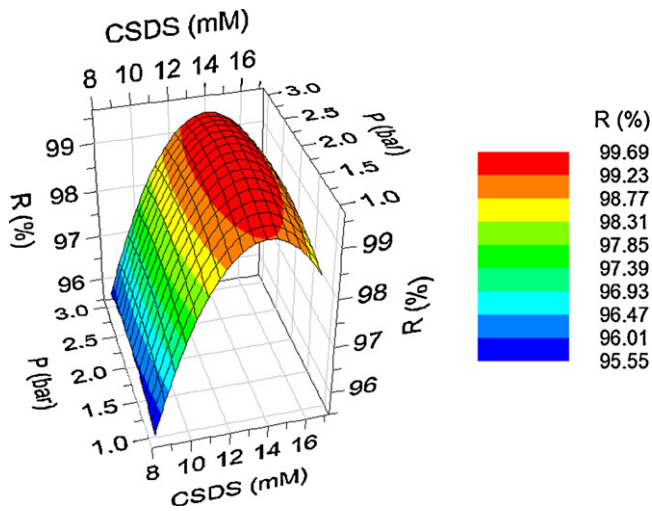


Fig. 3. Predicted retention values for the removal of zinc, spanned by the pressure (P) and SDS feed concentration (C_{SDS}) using the regenerated cellulose membrane of 5 kDa. The zinc feed concentration is 0.5 mM.

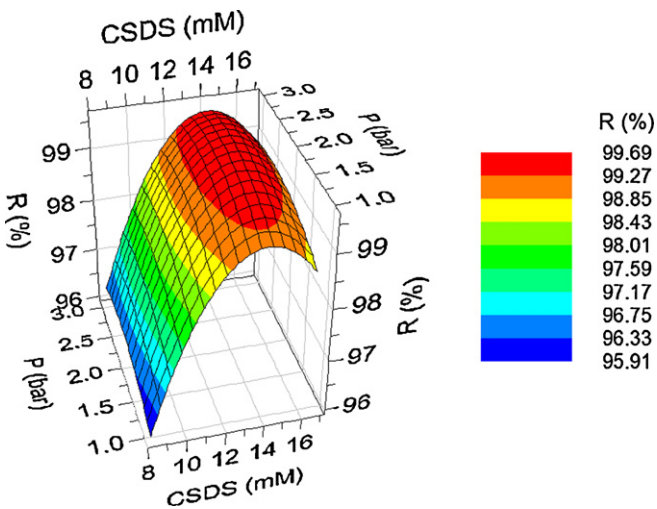


Fig. 4. Predicted retention values for the removal of cadmium, spanned by the pressure (P) and SDS feed concentration (C_{SDS}) using the regenerated cellulose membrane of 5 kDa. The cadmium feed concentration is 0.5 mM.

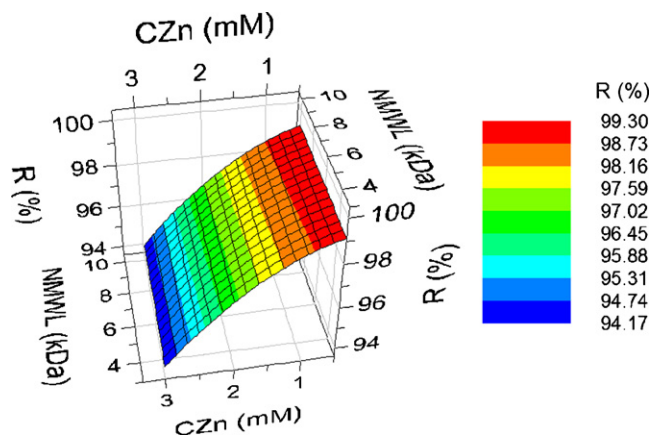


Fig. 5. Predicted retention values of zinc, spanned by the NMWL and zinc feed concentration. The SDS feed concentration is 12.5 mM and the pressure used is 3 bar.

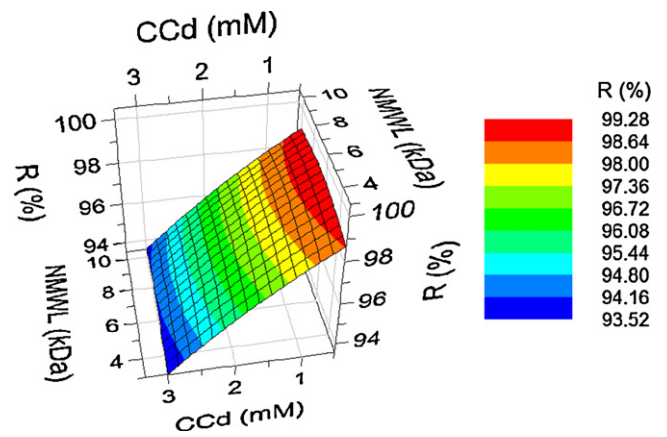


Fig. 6. Predicted retention values of cadmium, spanned by the NMWL and cadmium feed concentration. The SDS feed concentration is 12.5 mM and the pressure used is 3 bar.

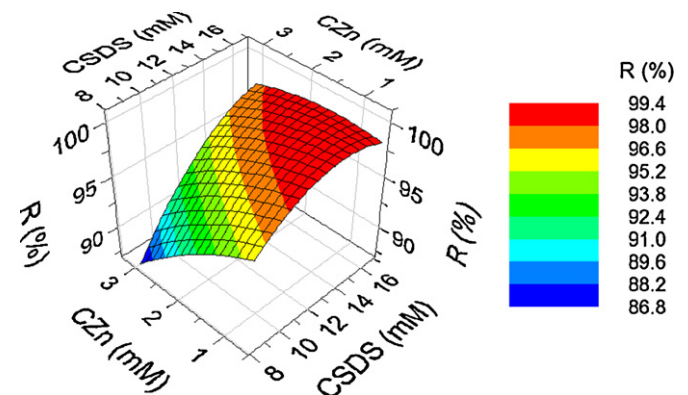


Fig. 7. Predicted retention values of zinc, spanned by zinc and SDS surfactant feed concentration. The regenerated cellulose membrane and the pressure used were 5 kDa and 3 bar, respectively.

predicted by the model, Q^2 , is 0.914. For the case of cadmium removal R^2 , R^2_{adj} and Q^2 are 0.966, 0.993 and 0.986, respectively. These results are very satisfactory and thus, the model validity is good.

3.2.2. The effects of factors on the heavy metal retention

3.2.2.1. The effect of pressure and NMWL on the retention of heavy metals. This study showed that NMWL and pressure had negligible effect on the retention of zinc and cadmium. On the contrary,

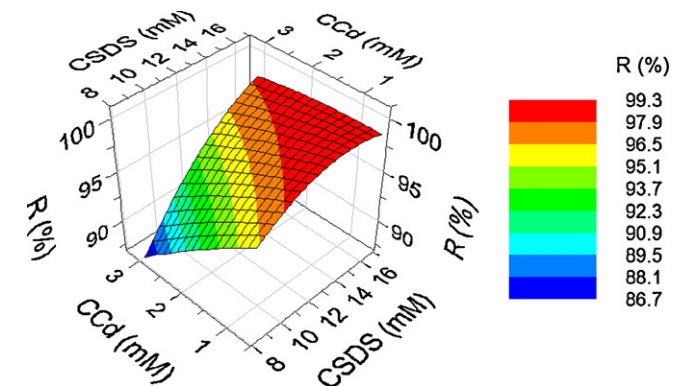


Fig. 8. Predicted retention values of cadmium, spanned by cadmium and SDS surfactant feed concentration. The regenerated cellulose membrane and the pressure used were 5 kDa and 3 bar, respectively.

Table 8

Experiments conducted at optimal conditions using 10 kDa membrane and pressure of 3 bar.

Metal	C _{SDS} (mM)	C _{metal} (mM)	S/M	R _{predicted} (%)	R _{observed} (%)	J _{predicted} (dm ³ /m ² h)	J _{observed} (dm ³ /m ² h)
Zn	13.9	0.5	27.8	99.5 ± 1.6 ^a	98.0 ± 0.4	70.1 ± 2.1	68.8 ± 1.4
Cd	14.2	0.5	28.4	99.4 ± 0.8 ^a	99.0 ± 0.2	70.5 ± 4.3	66.6 ± 3.5

^a The upper limit is not constrained.

previous studies observed that NMWL and pressure show significant effect on the rejection coefficient of heavy metals [11,27]. The effect of NMWL and pressure in retention of surfactant and heavy metals can be explained due to concentration polarisation. The gel formation due to concentration polarisation can contribute to a presieving effect increasing the retention of surfactant and heavy metals [11,28]. As explained in Section 3.1, in this study the concentration polarisation phenomenon was negligible. This might explain the insignificant effect of NMWL and pressure on the retention of zinc and cadmium.

3.2.2.2. Effect of surfactant feed concentration. Figs. 3 and 4 show the predicted retention values, spanned by the pressure and SDS feed concentration when heavy metal feed concentration is 0.5 mM. As it can be observed, at SDS feed concentration range of 8.3–14.0 mM, the higher SDS feed concentration, the higher retention of heavy metals is achieved. In addition, when SDS feed concentration is further increased to 16.6 mM no further increase in retention is observed. Therefore, increasing the SDS feed concentration enhances the retention of heavy metals until certain limits.

The maximum retention observed in Figs. 3 and 4 might be due to the competition of the surfactant sodium counter ions with the heavy metals. This explanation is corroborated with earlier reports [24,29,30]. The electrostatic interaction between the anionic micellar surface and the metal cations depends on the ion charge and concentration [30]. At first, when increasing the SDS feed concentration, a higher fraction of surfactants will be in micellar form. This will increase the surface charge; hence more divalent heavy metals will be adsorbed on the micellar surface displacing the sodium counter ions. This ion exchange will consequently enhance heavy metal retention. However, at diluted heavy metal feed concentration, when SDS concentration is further increased to concentration up to 16.6 mM, the sodium counter ion concentration might increase to an extent that the adsorption of sodium counter ions is favoured. Therefore, no further increase in heavy metal retention is achieved, as shown in Figs. 3 and 4.

3.2.2.3. Effect of heavy metal feed concentration. Figs. 5 and 6 show the predicted retention values, spanned by the NMWL and heavy metal feed concentration when SDS feed concentration is 12.5 mM. As it can be observed, the smaller the zinc feed concentration, the higher retention of heavy metals is achieved. When the heavy metal feed concentration is 0.5 mM, the retention achieved is up to 99%. However, at higher heavy metal feed concentration (3 mM) the retention drops to 94%. When increasing the heavy metal feed concentration the zeta potential of the micelles increases [24] as the surface charge density decreases. Therefore, the reduction in retention at higher feed concentration might be due to the lack of available binding sites, which, in turn can be explained by the increase in zeta potential [24,31]. Consequently, MEUF is more efficient in solutions with diluted metal concentrations, in contrast with traditional techniques such as precipitation, which are inefficient at dilute streams. MEUF could also be used in hybrid processing as a secondary treatment method.

3.2.2.4. The importance of surfactant to metal concentration ratio and interaction. From the results explained above it is clear that the effect of the SDS feed concentration on the heavy metal retention

depends on the heavy metal feed concentration, and vice versa. The importance of the factor interaction can be observed in Figs. 7 and 8. This dependence between surfactant and heavy metal feed concentrations has been widely described in the literature as the surfactant to metal concentration ratio (S/M) [10,27]. In order to find an efficient retention of heavy metals, the surfactant feed concentration has to be high enough to create micelles and to have enough available binding sites. However, the SDS concentration should not be too high either, where the adsorption of sodium counter ions is favoured. Thus, in order to find the maximum retention in the process optimisation, it is essential to find the optimum S/M.

3.3. Optimum S/M ratio for the heavy metals removal

A vital task in membrane process optimisation is to ensure maximum permeate flow whilst achieving maximum solute rejection [32]. Membrane durability and operational stability are also key factors in minimizing capital and operating costs. All the NMWL regenerated cellulose membranes used in this study had a good operational stability. Further, since concentration polarisation was negligible, high NMWL membranes with high pressure provided maximum flux, with negligible effect on the retention of heavy metals. The maximum flux is assured using 10 kDa RC membrane and pressure of 3 bar. Further, the optimum S/M ratio assured the maximum retention of zinc and cadmium from their respective mixture solutions. Therefore, when running the optimiser, the optimal conditions were characterised by maximising the retention of heavy metals using 10 kDa membrane and pressure of 3 bar. The predicted responses are summarized in Table 8. In the range studied the optimal S/M ratios obtained for the removal of zinc and cadmium are 27.8 and 28.4, respectively. These results are comparable to the results reported by Yurlova et al. [27] who observed a maximum retention of nickel when S/M ratio was 21.

The predicted difference between the optimal S/M ratios for the removal of zinc and cadmium is small. This is understandable since the empirical models obtained for each metal are very similar. As explained in Section 3.2.1, this might be because the metal valence is the dominant characteristic determining the separation efficiency in MEUF when removing multivalent inorganic metal ions from water [20].

Predicted responses were experimentally verified by performing experiments under the optimal conditions. As it can be observed in Table 8, the observed retention values are consistent with the predicted values showing the validity of the empirical models.

3.4. Recovery of SDS

In the first step of the surfactant recovery process, CaCl₂ is added in order to precipitate the surfactant as calcium dodecyl sulfate. In this study ten times the stoichiometric amount of CaCl₂ was added to the retentate sample. This amount was chosen in order to achieve 99% precipitation based on the solubility product constant (K_{sp}), as reported by Brant et al. [33]. In this study, 98% of precipitation was achieved. The result is satisfactory and in agreement with the results expected. In the second step, Na₂CO₃ solution is added to the precipitate stoichiometrically. In this step, 86% of the surfactant was redissolved as SDS. Therefore, the recovery process resulted in a 19.6 mM SDS solution. Taking into account the starting SDS reten-

tate concentration (23 mM), a total recovery of 84.6% was achieved, which is very satisfactory.

4. Conclusions

This study shows that RSM can be successfully applied to improve the efficiency of MEUF in the removal of zinc and cadmium from diluted streams. Further, response surface methodology is shown to be a useful method for modelling and optimisation of the process. In this study, concentration polarisation was concluded to be negligible using regenerated cellulose membranes. Therefore, maximum permeate flux with good membrane operational stability is concluded to be achieved using the highest NMWL membrane and highest pressure. Further, the importance of finding a compromise between surfactant and heavy metal feed concentrations (S/M ratio) in the optimisation stage was also proven. In the experimental region studied, the optimal conditions of the removal of zinc were concluded to be $C_{Cd} = 0.5$ mM, $C_{SDS} = 14.2$ mM, $NMWL = 10$ kDa and $P = 3.0$ bar. In the case of the removal of cadmium the opti-

mal conditions were $C_{Zn} = 0.5$ mM, $C_{SDS} = 13.9$ mM, $NMWL = 10$ kDa and $P = 3.0$ bar. The optimal S/M ratios obtained for the removal of zinc and cadmium are 27.8 and 28.4, respectively. The responses obtained experimentally at the optimal conditions were consistent with the predicted values, proving the good validity of the models developed by RSM approach. To improve resource efficiency, the surfactant was reclaimed after use; 84% of the initial SDS was recovered by precipitation. These results will be used in designing a MEUF-based methodology for the treatment of dilute heavy metal containing industrial wastewaters.

Acknowledgements

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Appendix A.

Experiment number	Factors				Responses	
	$C_{SDS} = X_1$ (mM)	$C_{Zn} = X_2$ (mM)	$NMWL = X_3$ (kDa)	Pressure = X_4 (bar)	R (%)	J_V (dm ³ /m ² h)
1	–	–	–	–	96.5	3.0
2	+	–	–	–	98.5	3.8
3	–	+	–	–	85.8	4.4
4	+	+	–	–	97.09	4.2
5	–	–	+	–	95.2	18.3
6	+	–	+	–	98.0	20.2
7	–	+	+	–	86.8	18.1
8	+	+	+	–	97.5	18.9
9	–	–	–	+	95.8	14.8
10	+	–	–	+	98.7	14.3
11	–	+	–	+	86.5	14.6
12	+	+	–	+	97.1	14.4
13	–	–	+	+	95.1	69.1
14	+	–	+	+	99.4	67.2
15	–	+	+	+	86.4	71.0
16	+	+	+	+	98.1	66.0
17	–	0	0	0	93.6	25.8
18	+	0	0	0	98.9	23.6
19	0	–	0	0	98.9	23.8
20	0	+	0	0	96.1	24.0
21	0	0	–	0	97.8	17.3
22	0	0	+	0	97.8	50.7
23	0	0	0	–	97.7	12.2
24	0	0	0	+	98.2	36.5
25	0	0	0	0	92.8	27.2
26	0	0	0	0	97.8	27.6
27	0	0	0	0	95.0	24.0

Appendix B.

Experiment number	Factors				Responses	
	$C_{SDS} = X_1$ (mM)	$C_{Cd} = X_2$ (mM)	NMWL = X_3 (kDa)	Pressure = X_4 (bar)	R (%)	J_V (dm ³ /m ² h)
1	–	–	–	–	96.1	9.3
2	+	–	–	–	98.9	7.1
3	–	+	–	–	86.4	6.0
4	+	+	–	–	98.1	5.8
5	–	–	+	–	94.7	19.4
6	+	–	+	–	98.2	16.6
7	–	+	+	–	84.9	19.5
8	+	+	+	–	96.9	16.1
9	–	–	–	+	96.2	24.0
10	+	–	–	+	98.3	24.7
11	–	+	–	+	86.1	25.2
12	+	+	–	+	97.2	27.0
13	–	–	+	+	95.9	70.6
14	+	–	+	+	98.5	65.3
15	–	+	+	+	86.9	68.6
16	+	+	+	+	98.1	67.5
17	–	0	0	0	91.2	27.3
18	+	0	0	0	98.5	23.6
19	0	–	0	0	98.9	23.5
20	0	+	0	0	94.5	25.2
21	0	0	–	0	96.0	24.4
22	0	0	+	0	96.1	60.8
23	0	0	0	–	96.0	14.7
24	0	0	0	+	96.2	34.8
25	0	0	0	0	97.2	26.7
26	0	0	0	0	97.4	25.0
27	0	0	0	0	97.3	24.9

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