

Removal of lead ions from aqueous solutions using the micellar-enhanced ultrafiltration process: Response surface methodology optimization

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Abstract

In this study, the micellar-enhanced ultrafiltration (MEUF) separation process was employed to determine the removal percentage of lead ions from aqueous solutions. The effect of diverse parameters, such as the initial concentration of lead (200-400 mg/l), operating pressure (2-4 bar) and molar concentration ratio of the surfactant SDS to the metal (5-10), was investigated using the Box-Behnken design (BBD) of response surface methodology (RSM). The number of experiments designed by this scheme was 15 and the importance of the effective parameters and their binary interactions were evaluated using the analysis of variance (ANOVA). The obtained results showed that the proposed model has optimal accuracy and efficiency in the prediction of the lead rejection percentage. The responses predicted by the model showed that the MEUF process could lead to a high rejection rate of Pb(II) ions (99.90 %) at optimal conditions.

Keywords: Lead, Surfactant, Membrane processes, Micellar-enhanced ultrafiltration, Optimization

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1. Introduction

Fresh and potable water for human consumption constitutes only three percent of the total water on the planet Earth, and the rest is spread in seas, polar ice, glaciers and soils [1-3]. Therefore, the high consumption of water in industries, on the one hand, and the pollution that exists in the effluents of factories, on the other hand, has made most of the researchers try to purify the output of the processes and return the treated water to the production cycle by removing the contaminants and their proper disposal [4-5]. Currently, the removal of heavy metals is one of the main challenges in the field of wastewater. Lead is one of the heavy metals that is most commonly employed in various industries, such as electroplating, paint, storage batteries, pesticides, and chemical fertilizers [6-7]. The main toxicity and risk of heavy metals for human health and living organisms are mainly related to their accumulation in the food chain [8]. Lead can enter the body through swallowing, inhalation, or skin absorption and target the nervous system, kidney, respiratory or digestive system, and skin [9]. This metal can be found in many wastewater effluents at 200–500 mg/l concentrations, while the permissible concentration limit set for it by the Environmental Protection Agency (EPA) is around 0.05 mg/l [10]. To remove this metal, various techniques such as ion exchange [11], adsorption [12-14], chemical precipitation [15-16] and solvent extraction [16-17] can be used. Each of these methods has disadvantages, which can be mentioned as their high expenses, excessive energy consumption, toxicity and contamination of the environment, and also the generation of vast quantities of secondary wastewater [18]. Membrane technologies are another way to remove heavy metals from wastewater, which have grown significantly in the last two decades due to some advantages such as lower energy and space requirements, less cost, higher separation efficiency in dilute solutions and ecologically friendly [19]. Among the membrane separation processes, ultrafiltration membranes have attracted special

attention due to their higher permeability flux and lower energy usage. The most significant drawback of these membranes is that they are not able to separate components with small molecular weights, and passing through the membrane pores is easy for metal ions with a small hydrated radius [20].

The micellar-enhanced ultrafiltration (MEUF) process is a separation method based on the combination of surfactants and ultrafiltration membranes, which is used to remove organic compounds, low molecular weight components, and transition metals from aqueous solutions [21-22]. After adding a surfactant to the pollutant phase, surfactant monomers accumulate and, at a concentration equal to the critical micelle concentration (CMC), create micelles with a diameter larger than the pores of the ultrafiltration membrane [23]. Micelles can facilitate the dissolution of organic substances and interact with pollutants due to their different surface charge. Through the effective separation of metal ions with high efficiency, the MEUF process serves to enhance the performance of the ultrafiltration membranes by ensnaring small-sized pollutants inside the micelles [24].

Lee and Shrestha investigated the removal of zinc ions from synthetic wastewater using the MEUF process. According to their research, a slight reduction in the elimination percentage of this metal can occur when the initial concentration of zinc ions is increased while maintaining a constant SDS content [25]. Rahmanian et al. used two models of feed-forward artificial neural network (ANN) and adaptive neuro-fuzzy inference system (ANFIS) to predict the performance of the MEUF process in the removal of lead metal from aqueous solutions. The results of their simulation showed that the ANFIS model, compared to the ANN model, is able to provide more reliable results for the two responses of permeate flux and lead removal percentage [26].

The aim of this study is to remove lead metal from aqueous solutions using the MEUF process and optimize the parameters affecting it using the response surface methodology (RSM) and Box-Behnken design (BBD). The parameters investigated in this process are the initial concentration of lead metal, the operating pressure and the molar concentration ratio of the surfactant SDS to the metal (SDS/M). The effect of the initial concentration of lead ions, the operating pressure and their interactions on removing this metal has not been investigated so far with the help of the MEUF process.

2. Experimental

2.1. Materials

In this study, lead chloride (PbCl_2) with a molecular weight of 278.10 g/mol and sodium dodecyl sulfate anionic surfactant ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$, SDS) with a CMC equal to 8.3 mM were both purchased from Merck, Germany. Double distilled water was used to make the solutions in all experiments. The commercial ultrafiltration membrane employed was polyethersulfone (PES) with a 10-kDa molecular weight cut-off (UE10 Series), which was obtained from Sterlitech Corporation.

2.2. MEUF experiments

Separation of lead ions from the artificial wastewater made utilizing lead chloride salt was performed in a batch membrane ultrafiltration system with an effective membrane surface area of 0.00331 m^2 . The general schematic of this system is shown in Figure (1). The body of the filtration cell was built of polycarbonate to be highly resistant to corrosion and pressure. All device connections were made of stainless steel 316, and a magnetic stirrer (Alfa, model HS-860) with a speed of 1800 rpm was used for complete mixing and preventing concentration polarization. Ultrafiltration experiments were performed at room temperature and pressures of 2-4 bar. Nitrogen

gas was employed to provide the pressure difference and driving force of the process. The PES membranes were first fully compressed at 3 bar for 30 minutes, and after achieving a uniform pure water flux, the filtration tests were initiated. Each of the prepared feed solutions was stirred for 30 minutes at a constant speed by a magnetic stirrer. Sampling was done when the volume of the permeate solution reached one-third of the feed solution volume. Inductively coupled plasma (ICP) spectrometry was employed to measure the lead ion concentration in the permeate phase. After each MEUF experiment, the membrane surface was washed and the distilled water flux passing through the membrane was re-measured and compared with the water flux of the neat membrane. The used membrane was replaced if a difference of more than 5 % was observed between the two measured fluxes [24].

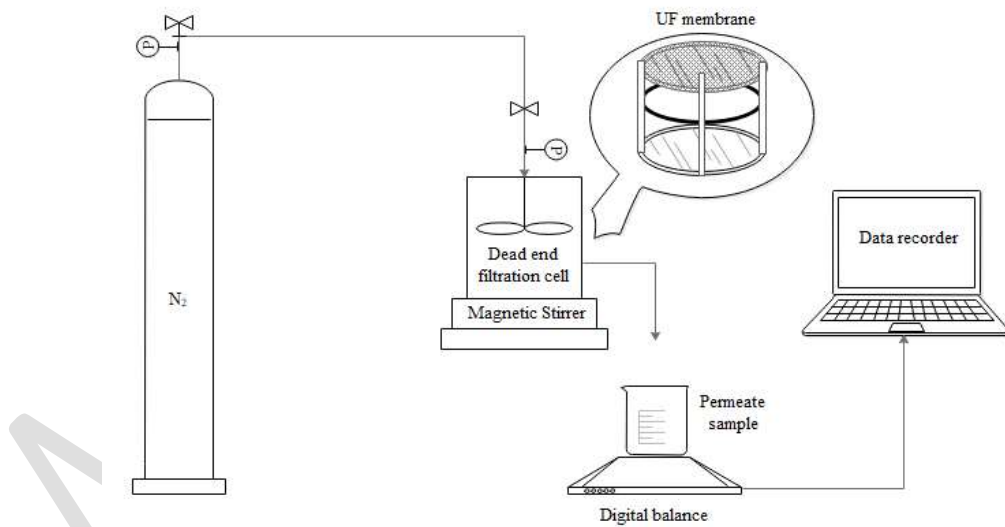


Figure (1): Schematic of the batch ultrafiltration system used on a laboratory scale

The volumetric flux passing through the membrane ($\frac{l}{m^2.h}$: LMH) was calculated according to the following equation to be compared with the neat membrane:

$$J = \frac{V}{A \times \Delta t} \quad (1)$$

where V is the total permeate volume (l), A is the effective membrane surface area (m²) and Δt is the sampling duration (h) [27]. The metal percentage rejected by the ultrafiltration membrane in the MEUF system can also be calculated through equation (2).

$$\%R = 1 - \frac{C_p}{C_F} \quad (2)$$

where C_P and C_F represent the lead ions concentrations in mg/l for the permeate stream and feed solution, respectively [28].

2.3. Experimental design

In this study, the response surface methodology was used to extract the mathematical model, find the parameter with the most significant effect and optimize the test conditions. This method creates the test matrix by determining the number of variables and the maximum and minimum limits for each parameter. After the initial screening of the variables and determining their optimal limits, the relationship between the independent variables and the responses can be obtained by fitting the experimental data with the following model:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_{ii}^2 + \sum_{i=1}^k \sum_{i \neq j=1}^k \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

In the above equation, Y represents the predicted response, k is the number of independent parameters and β₀ is a constant value. β_i, β_{ii} and β_{ij} demonstrate the coefficients related to linear, quadratic and mutual effects, respectively. The amounts of x_i and x_j also show the encoded values of the independent parameters [29].

In this research, to ascertain the impact of operational factors on the performance of the MEUF process in the removal of lead ions, the BBD design was used and the effect of various parameters such as initial concentration of lead metal, operating pressure and SDS/M ratio was studied. The design of experiments was done with the help of Stat-Ease, Design-Expert 13 software, and the studied variables, along with the three levels considered for them, are shown in Table (1).

Table (1): Independent variables and their levels in BBD scheme used in this research

Variables	Unit	Code	Levels		
			-1	0	1
Lead concentration	mg/l	A	200	300	400
Pressure	bar	B	2	3	4
SDS/M	----	C	5	7.5	10

3. Results and discussion

3.1. Statistical analysis

As shown in Table (2), the number of experiments designed using the BBD scheme with three central points is equal to 15 experiments.

Table (2): Experiments designed with the help of BBD scheme

Run number	Lead concentration (mg/l)	Pressure (bar)	SDS/M
1	300	3	7.5
2	200	4	7.5
3	300	3	7.5
4	400	4	7.5
5	400	3	5
6	300	2	10
7	200	2	7.5
8	200	3	10
9	400	2	7.5
10	400	3	10
11	300	3	7.5
12	300	4	10
13	300	2	5
14	300	4	5
15	200	3	5

Analysis of variance (ANOVA) was used to analyze the obtained results and find out to what extent the presented model matches the data obtained from the experiments. To determine the correctness of the selected model, the p-value of the important and influencing factors on the output results was examined. Based on the assumptions in the software, if the amount of this parameter is less than 0.05, the selected model is correct and the input factors will have a major impact on the output results. The efficiency of the model was expressed by the coefficient of determination (R^2) and its statistical significance was determined by the Fisher test (F-Value). It should be noted that the coefficient of determination alone cannot express the accuracy of the model, because this

index represents the changes around the average response. Therefore, another coefficient called the adjusted coefficient of determination ($R_{adj.}^2$) is also used. For high-performance models, the value of this parameter should be slightly different from the coefficient of determination. The predicted coefficient of determination ($R_{pred.}^2$) should also be close to the adjusted coefficient of determination and have a difference of less than 0.2 [30].

Table (3): Analysis of variance for the response of lead rejection

Source	Sum of Squares	DF	Mean Square	F-Value	p-value	
Model	0.0205	6	0.0034	18.94	0.0005	Significant
A-Concentration	0.0061	1	0.0061	33.55	0.0007	
B-Pressure	0.0023	1	0.0023	12.80	0.0090	
C-SDS/M ratio	0.0050	1	0.0050	27.94	0.0011	
AB	0.0002	1	0.0002	0.8650	0.3833	
AC	0.0015	1	0.0015	8.27	0.0238	
BC	0.0019	1	0.0019	10.48	0.0143	
Residual	0.0013	7	0.0002			
Lack of Fit	0.0007	5	0.0001	0.4319	0.8058	Not significant
Pure Error	0.0006	2	0.0003			
Cor. Total	0.0218	13				

The F-value index shows the effect of the variable on the response, and the higher its value, the greater the influence of that variable on the response. As can be seen in Table (3), the order of influence of the variables on the percentage of lead removal using the MEUF process can be arranged as $A > C > B > BC > AC$. AB is also not considered among the variables affecting the process due to having a p-value > 0.05 . Considering the non-significance of the lack of fit parameter, or in other words, having a p-value greater than 0.05 of this parameter, it can be concluded that the presented model has sufficient accuracy for fitting the experimental data. As reported in Table (4), the values of R^2 , R^2_{adj} , and R^2_{pred} , also confirm the effectiveness of the presented model and its good predictive ability. The fact that the standard deviation is smaller than ten percent of the average value and the coefficient of variation (CV) is slighter than ten percent indicates the desirability of the presented model. A value greater than 4 for the adequate precision index also shows the high accuracy of the model in the prediction of data. The numerical value of the predicted residual error sum of squares (PRESS) was also equal to 0.0047. The smaller this parameter is, the closer the predicted values will be to the actual values.

Table (4): Statistical parameters used in the evaluation of the presented model

Statistical parameter	Value	Statistical parameter	Value
Standard deviation	0.0134	R^2	0.9420
Mean	99.860	R^2_{adj}	0.8922
CV (%)	0.0135	R^2_{pred}	0.7827
PRESS	0.0047	Adequate precision	13.259

The two-factor interaction (2FI) model was used to predict the lead rejection percentage based on the coded parameters in equation (4). The magnitude of each parameter coefficient confirms the order of influence presented for the variables. Relying on this concept, the concentration of lead ions, SDS/M ratio and operating pressure have the most positive effect on the rejection of this metal, respectively.

$$\% R = 99.86 + 0.0312A + 0.017B + 0.0285C - 0.0062AB - 0.0243AC - 0.0217BC \quad (4)$$

Residual analysis was employed to further investigate the efficiency of the proposed model. According to the normal probability plot of the residuals, Figure (2-a), the errors related to the lead removal percentage are normally distributed due to the location of the majority of the residuals in the vicinity of the straight line. Based on Figure (2-b), the values of the residuals do not follow a specific pattern and indicate the effectiveness of the suggested model. As shown in Figure (2-c), no specific relationship is observed between the data and as a result, the errors are independent of each other. Figure (2-d) also shows the ability of the model to predict new responses, considering the low deviation of most points from the 45-degree line.

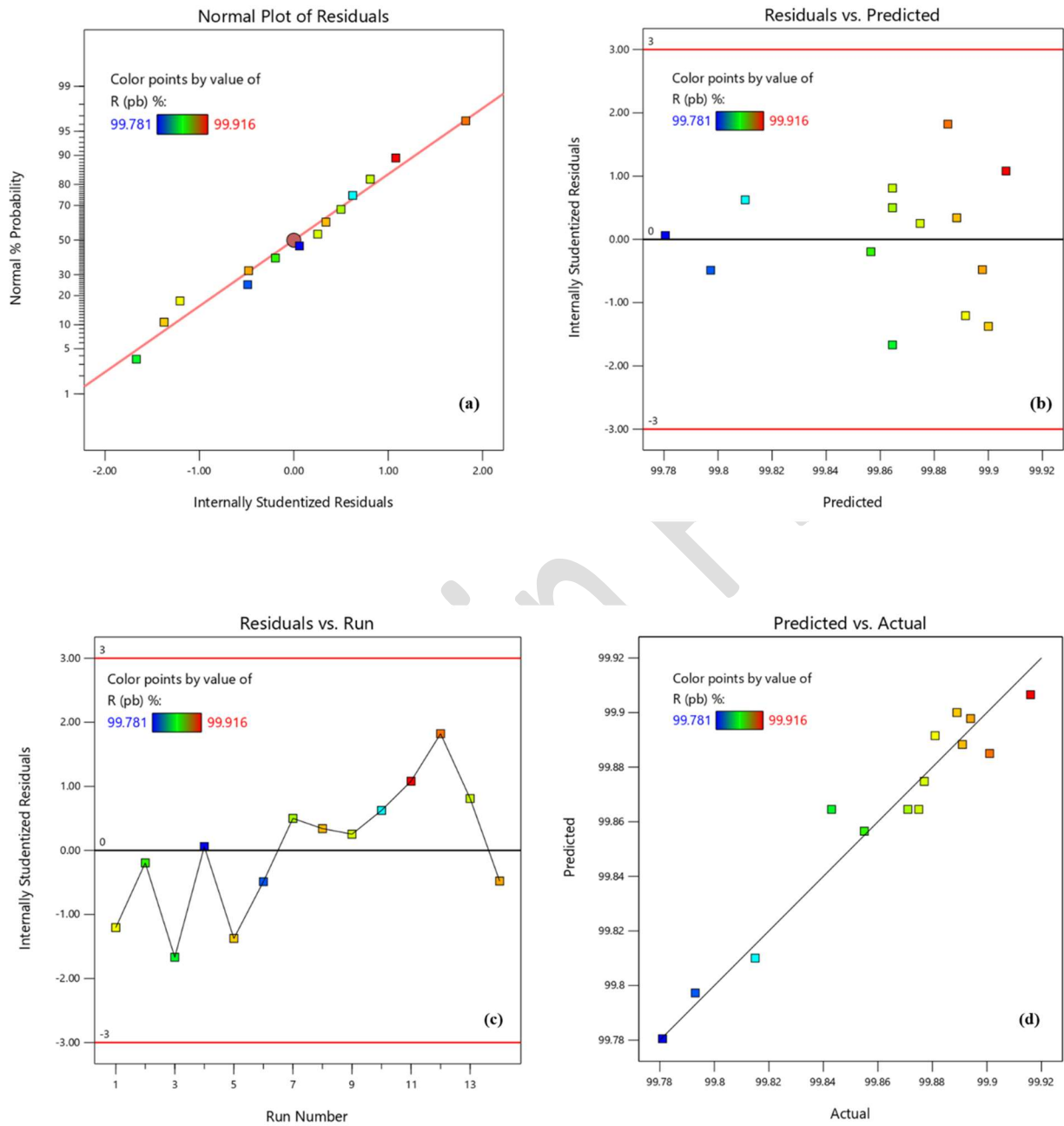


Figure (2): The residual analysis for the response of lead rejection; a) normal probability plot of the residuals, b) plot of residuals versus the predicted values, c) plot of residuals versus run order, d) plot of predicted values versus the actual values

3.2. The mutual effects of different parameters on the percentage of lead rejection

In Figure (3-a), the mutual effect of lead concentration and SDS/M parameters on the percentage of lead rejection is shown as a three-dimensional diagram, in which the operational pressure was kept constant at its central level. Based on this figure, with the increase of the SDS/M ratio at the lowest level of lead metal concentration, the removal percentage of this metal increases slightly. The reason for this increase can be attributed to the rise in the number of active sites of the surfactant for binding to the metal ions. While at the high concentration of this metal, the effect of increasing the SDS/M ratio on the response variable is insignificant. Also, increasing the concentration of lead metal at low levels of the SDS/M ratio has a greater effect on increasing the removal percentage of this metal. Figure (3-b) also shows the simultaneous effect of pressure and SDS/M parameters on the lead rejection. In this case, the metal concentration was considered constant at its central level. According to this figure, increasing the SDS/M ratio at the lowest pressure level causes a greater increase in the percentage of lead rejection, and increasing the pressure at the minimum level of SDS/M has a higher influence on the response variable.

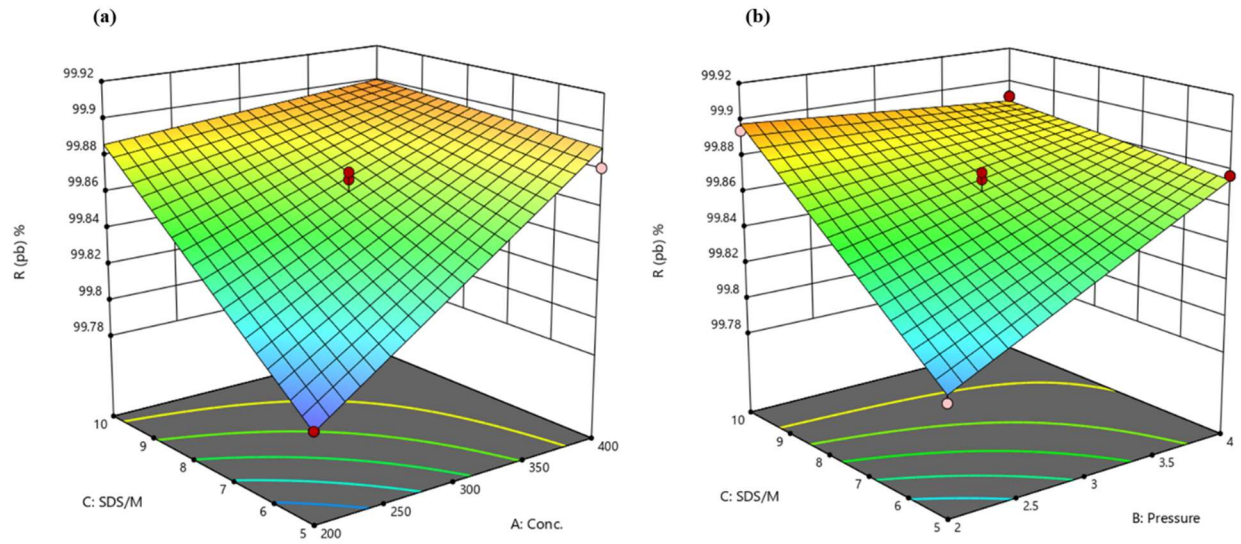


Figure (3): The mutual effects of different parameters on the percentage of lead rejection; a) Interaction of metal concentration and SDS/M ratio, b) Interaction of pressure and SDS/M ratio

3.3. Optimization of the variables

The optimal levels of the variables were adjusted in such a way that the maximum removal percentage of lead ions was obtained. The results of this optimization, along with the response predicted by the proposed model, are presented in Table (5). The introduced optimal test was also investigated experimentally and the percentage of lead rejection was obtained as 99.92%, which is in very good agreement with the response predicted by the model at optimal levels of parameters.

Table (5): The optimal conditions determined using the RSM method

Concentration (mg/l)	Pressure (bar)	SDS/M	R (Pb²⁺) %
400	3.96	7.98	99.90

4. Conclusions

In this research, the performance of the MEUF process in removing lead ions from aqueous solutions was investigated utilizing the SDS surfactant and optimization of the parameters affecting the process. The ANOVA results illustrated that the initial concentration of lead metal is the most influential parameter on the lead removal percentage by this process. The optimal conditions for the parameters such as initial lead concentration, operating pressure and SDS/M ratio in the MEUF process and with the help of BBD design were estimated as 400 mg/l, 4 bar and 8, respectively. Based on this, the rejection percentage of lead ions reached 99.90 % in the optimal conditions of the process. According to the obtained results, increasing the SDS/M ratio at the lowest level of pressure and also increasing the pressure at the minimum level of SDS/M showed a more significant influence on the lead rejection percentage.

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