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Arsenic removal by the micellar-enhanced ultrafiltration using response surface methodology

Oznur Begum Gokcek and Nigmet Uzal

ABSTRACT

The present research investigates the removal of arsenic (As) from aqueous solutions using micellar-enhanced ultrafiltration (MEUF) by utilizing two different surfactants: benzethonium chloride and dodecyl pyridinium chloride (BCl and DPCl). The impact of the operating variables and maximum removal efficiency were found under different conditions for BCl and DPCl surfactants. The maximum As rejection efficiency for MEUF with BCl and DPCl surfactants is 92.8% and 84.1%, respectively. In addition to this, a statistics-based experimental design with response surface methodology was used for the purpose of examining the impact of operating conditions, including initial pH, initial As concentration (ppb), and surfactant concentration (BCl, mM) in As-removal from aqueous solutions. In the analysis of the experimental data, a second-order polynomial model that was validated by statistical analysis for the BCl surfactant was used. On the basis of the response model created, the removal of As ions was acquired at optimum operating parameters, including the initial As concentration of 150 ppb, surfactant concentration of 5 mM and pH 10 for the BCl surfactant with 92.8% As-removal efficiency.

Key words | arsenic, complexation, heavy metal, micellar-enhanced ultrafiltration, response surface methodology

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INTRODUCTION

As a result of population growth, rapid urbanization and industrial activities, the demand for fresh water is increasing with each passing day. In addition to limited water resources, deterioration of water quality constitutes a significant threat to human health. Over time, arsenic (As), which is among the most hazardous contaminants in drinking water, has become an important parameter in monitoring pollution of water resources and identifying the quality of drinking water. As can cause serious health issues, including cardiovascular, respiratory, genotoxic, and gastrointestinal diseases, and it also has a mutagenic and carcinogenic impact. The allowable maximum concentration of As in drinking water was determined as 10 ppb by the World Health Organization in 1993 (Zaw & Emett 2002; Hung Nekrassova & Compton 2004). These stringent standards have led to a necessity for more effective As-removal technologies. However, conventional treatment methods cannot satisfy the drinking water standards in terms of As. Various treatment processes, such as coagulation (Song *et al.* 2006; Pallier *et al.* 2010; Shaoxian & Marisol 2014; Bora *et al.* 2016), adsorption (Iesan *et al.* 2008; Zhu *et al.* 2009; Zhou *et al.* 2017; Hao *et al.* 2018), membrane separation (Sato *et al.* 2002; Qdais & Moussa 2004; Ergican Geocol & Fuchs 2005; Figoli *et al.* 2010; Hao *et al.* 2018; Zhang *et al.* 2018; Kumar *et al.* 2019), precipitation/co-precipitation (Baskan & Pala 2009; Sorlini Gialdini & Collivignarelli 2014), and biological processes (Katsoyiannis & Zouboulis 2004; Wang *et al.* 2016; Le Pape *et al.* 2017), have been presented for the removal of As from water.

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Among the physical treatment methods, membrane separation is one of the most efficient and promising techniques approved for As-removal. Reverse osmosis (RO) and nanofiltration (NF) have been suggested as the most effective methods for removing more than 95% of As from contaminated groundwater (Harisha *et al.* 2010; Sen Manna & Pal 2010; Criscuoli & Figoli 2018). However, adopting RO and NF, which consume a lot of energy, is difficult in developing countries because of economic problems. Moreover, there are much more important problems in NF/RO membranes with regard to membrane fouling originating from colloidal deposition, biological growth, and inorganic precipitation. For the purpose of eliminating the mentioned deficiencies, there is a need for complex pretreatment and some other additional operational techniques. Therefore, ultrafiltration (UF) and microfiltration (MF) seem to be more advantageous for the treatment of wastewater since they provide high fluxes at comparatively low pressures but are not able to separate As directly. It is crucial to select the most appropriate membrane process for As-removal technically and economically (Bielska & Prochaska 2007; Zhang *et al.* 2018). At this point, to enhance the performance of UF, micellar-enhanced ultrafiltration (MEUF) can be employed for the removal of As from the aqueous phase (Gecol Ergican & Fuchs 2004; Katsoyiannis & Zouboulis 2004; Iqbal *et al.* 2007; Molinari & Argurio 2017; Chen *et al.* 2018).

MEUF represents a separation technique that includes the addition of a surfactant for the purpose of increasing the size of the pollutant molecules by creating a complex of surfactant micelles and pollutants. The surfactant used in MEUF forms micelles at a surfactant concentration above the critical micelle concentration (CMC). Above CMC, surfactant monomers start to assemble micelles with aggregate diameters considerably higher than the pore diameter in the ultrafiltration membrane. The pollutants are bound to the micelles and form micelle heavy metal complexes, and the complexes are sufficiently large to inhibit their passing through an ultrafiltration membrane (Baek Kim & Yang 2003; Baek & Yang 2004; Bielska & Prochaska 2007). As-removal from water by utilizing surfactant micelles and ultrafiltration membranes was examined by Gecol *et al.* (2004). In this study, the efficiency of different types of UF membranes (regenerated cellulose and polyethersulfone) was tested using cetylpyridinium chloride (CPC) as a surfactant. As a result of this study, As-removal was affected by feed water As concentrations, initial pH values, and the membrane materials used (Gecol Ergican & Fuchs 2004). In another As-removal study using CPC as a surfactant, the impacts of a number of operating factors on permeate flux were examined, and the experimental results showed that As-removal efficiencies were depending on the initial As concentrations. In addition to these studies, Iqbal *et al.* (2007) examined the As-removal performances of four different surfactants. The reported MEUF studies generally deal with one surfactant type and conventional methods of experimentation using one factor variable. For the purpose of improving the removal of As, an optimization approach should be employed to find out the optimal operating parameters for the efficient As-removal. Chen *et al.* (2018) evaluated and modeled As(V) removal from both synthetic solutions and spiked samples of natural water, by MEUF, using CPC to form the micelles. Monovalent arsenate was poorly removed, but >90% removal of divalent was achieved using >5 mM CPC in the absence of competing anions. A simplified model based on mass balances across UF membranes, selectivity coefficients determined from test results on binary systems, and As speciation as a function of pH was used to predict As(V) removal by MEUF. Response surface methodology (RSM) represents an efficient statistical tool to optimize heavy metal removals (Cojocaru & Zakrzewska-Trznadel 2007; Özer *et al.* 2009; Poroch-Seritan *et al.* 2011; SIk *et al.* 2017; Sahu Mahapatra & Patel 2018; Adlnasab Shekari & Maghsodi 2019). The primary benefit of RSM is the decreased number of experimental trials required for calculating complex interactions between the independent factors (Ahmad *et al.* 2009). Ferella *et al.* (2007) investigated As-removal from wastewater by utilizing dodecylbenzene sulfonic acid as an anionic surfactant and dodecylamine as a cationic surfactant. The process of UF is realized by molecular weight cut-off (MWCO) of 210 kDa. Five-day biological oxygen demand and chemical oxygen demand for As are removed from water at about an average rejection of 30%.

The aim of the current study was to examine the feasibility of the MEUF process combining two different surfactants (benzethonium chloride, BCl and dodecyl pyridinium chloride, DPCl) with UF membranes for treating

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As-contaminated water. A statistics-based experimental design with RSM was used for the purpose of examining the impact of operating conditions, including initial pH, initial As concentration, and surfactant concentration (BCl, mM), in As-removal from aqueous solutions.

MATERIAL AND METHODS

Chemicals

All the chemicals utilized in the experiments were of analytical reagent grade. Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4.7H_2O$, Mw = 312 g/mol, Sigma-Aldrich, India) was utilized for preparing aqueous solutions of As ions. Cationic surfactants, DPCl ($C_{17}H_{31}NCl$, Sigma, USA) and BCl ($C_{27}H_{42}NO_2Cl$, Sigma, Japan) were used in MEUF experiments. The CMC of the DPCl and BCl surfactants was determined as 2.45 mM and 1.47 mM, respectively, using the stalagmometric method (Taş 2006). Ultra-pure water was utilized to prepare all the feed solutions. Nitric acid and sodium hydroxide solutions of 0.2 and 0.02 M were utilized to adjust pH. The UF membranes utilized in the experiments were produced from regenerated cellulose with a MWCO of 3 kDa and 10 kDa (GE Osmonics, Germany).

Analytical methods

An Agilent 7500ce Inductively Coupled Plasma–Mass Spectrophotometer (ICP–MS), a device that combines a high-temperature ICP source with a mass spectrometer, was utilized for measuring the concentrations of As ions in feed and permeate solutions. To perform the pH measurements of the solution in the research, a Thermo Scientific, Orion 3 Star pH meter was utilized, while to perform the conductivity measurements, a Hach Lange HQd Field Case Multi Parameter was used.

MEUF experiments

MEUF experiments were carried out in a batch-stirred membrane cell (Amicon 8200, Millipore) with 3 kDa and 10 kDa (Millipore, USA) regenerated cellulose membranes to ensure the removal of micelles. The UF membrane's diameter was 44.5 mm with an effective area of 13.4 cm^2 used in dead-end filtration. The new membrane's water flux was approximately 62–70 L/m^2 h at 300 kPa of the applied pressure and at a room temperature of 25 ± 2 °C.

Surfactant was added to the feed As solution with an initial volume of 250 mL prior to filtration, and fixation of pH at the desired pH level was carried out. In every experiment, the solution was stirred in a gentle manner for approximately 1 h for the purpose of ensuring the complex formation. After the complexation step, 150 mL of feed solution was added to the dead-end filtration cell. The dead-end cell was stirred gently for the purpose of preventing the formation of concentration polarization. Dead-end MEUF experiments were conducted at a pressure of 300 kPa (43.5 psi) and a temperature of 25 ± 2 °C. Following every experiment, ultra-pure water was used to wash the membrane thoroughly, *in situ*. The dead-end cell channel was dismantled afterward and ultra-pure water was utilized to wash the membrane. The membrane cell was assembled again, and the membrane permeability was rechecked. The mentioned process allowed for the recovery of the pure initial water flux within 95%.

Design of experiments

RSM is an alternative statistical approach offering a large amount of information from a low number of experiments. The effect of the binary combination of independent parameters is easily explained by the RSM model equation.

The experimental design of the MEUF process was carried out for the BCl surfactant for the purpose of examining the impacts of operating conditions (initial As concentration (ppb), surfactant concentration (mM), initial pH of solution) on As retention. The central composite experimental design (CCD) was employed using Design Expert 7.0 for the response surface modeling and optimizing the As-removal process by MEUF. The CCD experimental design includes 16 experiments with eight orthogonal design points, six star points with $\alpha = 1.682$ and for the replication two center points. The experimental factors (design variables) considered are presented below: initial As concentration (ppb), surfactant concentration (mM), and initial pH of the aqueous solution. The ranges of the operating parameters and the levels of the

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Table 1 | Experimental design variables of the As-removal procedure by MEUF

Factors	Symbol	Actual values of the coded levels				
		$-\alpha$[a]	−1	0	1	$+\alpha$
Initial As concentration (ppb)	x_1	30.65	150	325	500	619.35
Surfactant concentration (mM)	x_2	0.98	2	3.5	5	6.02
Initial pH	x_3	1.95	4	7	10	12.05

[a]$\alpha = 1.682$.

independent and controllable variables investigated in the current research are presented in Table 1.

For the purpose of determining the mathematical correlation between the response and factors, the second-order polynomial equation presented below was utilized:

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

where Y refers to the predicted response, b_0 refers to the constant coefficient, b_i refers to the linear coefficients, b_{ij} refers to the interaction coefficients, b_{ii} refers to the quadratic coefficients, and X_i and X_j refer to the coded levels of the process factors examined. The model was fitted using multiple linear regressions, and analysis of variance (ANOVA) was conducted for testing the significance of the quadratic empirical RSM model. The confidence level was accepted as 95%.

Central composite designs are commonly utilized in statistical modeling for the purpose of acquiring response surface models setting the mathematical correlations between response and experimental variables. Therefore, the central composite orthogonal experimental design for three variables and response As rejection was given in Table 2.

The As rejection efficiency (Y%) was determined as follows:

$$Y = 1 - \frac{C_P}{C_f} \quad (2)$$

Table 2 | Central composite orthogonal design for three variables and experimental response of the MEUF process

Run number (N) and type[a]		Factors (controllable input variables)						Response	
		Initial As concentration		Surfactant concentration (mM)		Initial pH of solution		As rejection coefficient	
		$[As]_0$, ppb	Level[b] x_1	S	Level[b] x_2	pH	Level[b] x_3	BCI Y (%)	DPCI Y (%)
1	S1	325.00	0	3.50	0	1.95	$-\alpha$	19.3	6.72
2	S2	619.35	α	3.50	0	7.00	0	26.54	31.57
3	O1	500.00	1	2.00	−1	10.00	1	64.35	84.14
4	C1	325.00	0	3.50	0	7.00	0	30.1	30.11
5	O2	500.00	1	5.00	1	10.00	1	83.89	59.42
6	S3	325.00	0	6.02	α	7.00	0	66.32	26.18
7	S4	30.65	$-\alpha$	3.50	0	7.00	0	44.96	30.11
8	O3	150.00	−1	5.00	1	4.00	−1	33.26	24.82
9	S5	325.00	0	3.50	0	12.05	α	78.43	79.73
10	C2	325.00	0	3.50	0	7.00	0	30.01	28.11
11	S6	325.00	0	0.98	$-\alpha$	7.00	0	42.7	56.1
12	O4	500.00	1	5.00	1	4.00	−1	36.95	13.07
13	O5	150.00	−1	2.00	−1	4.00	−1	16.64	16.34
14	O6	150.00	−1	2.00	−1	10.00	1	60.6	71.05
15	O7	150.00	−1	5.00	1	10.00	1	92.81	63.6
16	O8	500.00	1	2.00	−1	4.00	−1	26.72	22.69

[a]O: orthogonal design points, C: center points, S: star or axial points.
[b]−1 = low value, 0 = center value, +1 = high value, +/−α = star point value.

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where C_f denotes the concentration of As in the feed solution (ppb) and C_P denotes the concentration of As in the permeate (ppb).

RESULTS AND DISCUSSION

Impact of initial As concentration on As-removal

The impact of initial As concentration on the As-removal efficiency for BCl and DPCl surfactants (surfactant conc: 5 mM and pH = 10) is summarized in Table 3. When the concentration of BCl surfactant was 5 mM and the initial concentration of As was 150 ppb, the As-removal efficiency was 92.8%. On the other hand, with an increase in the initial As concentration to 500 ppb, the As-removal efficiency decreased to 84%. When the concentration of DPCl surfactant was 5 mM and the initial concentration of As was 500 ppb, the As-removal efficiency was 63.6%, the initial As concentration increased to 500 ppb and the removal efficiency decreased to 59.4%.

When the results of the experiments given in Table 3 were evaluated based on the initial As concentration, two different surfactant concentrations (2 mM and 5 mM) and two different pH (between pH 4–10) values were evaluated, and the removal efficiencies at low pH and low initial As concentration were significantly reduced. At high surfactant concentration, BCl surfactant was found to be better than DPCl surfactant in terms of As-removal efficiency, whereas at low pH and low surfactant concentration, the removal efficiency of both surfactants was close to each other. Beolchini *et al.* (2007) in their study of 6–10 ppm As concentrations 93–98% and 70–74% removal efficiency were obtained, respectively.

Impact of surfactant concentration on As-removal

The experimental results of the impact of surfactant concentration on the As-removal efficiency is given in Table 4. As can be observed from Table 4, in MEUF experiments carried out with BCl surfactant at pH 10 and initial As concentration of 500 ppb, with an increase in the surfactant concentration from 2 mM to 5 mM, the As-removal efficiency increased by 20%. On the other hand, a decrease from 84.1% to 59.4% occurred in the removal efficiency for DPCl surfactant with an increase in surfactant concentration for the same operating conditions. For the initial As concentration of 150 ppb and pH 4, similar results were obtained for both surfactants tested. As can be clearly observed from Table 4, in the experiments performed at pH 4 and 10, an increase in the surfactant concentration for BCl surfactant increased the As-removal efficiency. On the other hand, it was determined that an increase in the surfactant concentration for DPCl surfactant decreased the As-removal efficiency. The CMC value of the DPCl surfactant is higher than the BCl surfactant and is higher than the experimental working range of 2 mM whilst the removal efficiency of the DPCl surfactant is lower. Similar results were also observed in studies conducted by Beolchini *et al.* (2007); Iqbal *et al.* (2007).

For BCl surfactant, the increase in surfactant concentration increased the As-removal while the initial As concentration was 500 ppb and pH 10, whereas the decrease in As-removal with the increase in surfactant concentration

Table 3 | The impact of initial As concentration on As-removal

	As (ppb)	Surfactant (mM)	pH	As-removal (%)
BCl	150	5	10	92.8
	500	5	10	84.0
DPCl	150	5	10	63.6
	500	5	10	59.4
BCl	150	2	4	16.6
	500	2	4	26.7
DPCl	150	2	4	16.3
	500	2	4	22.7

Table 4 | The impact of surfactant concentration on As-removal

	As (ppb)	Surfactant (mM)	pH	As-removal (%)
BCl	500	2	10	64.4
	500	5	10	84.0
DPCl	500	2	10	84.1
	500	5	10	59.4
BCl	150	2	4	16.6
	150	5	4	33.3
DPCl	150	2	4	16.3
	150	5	4	24.8

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was the same conditions for the DPCl surfactant. At the initial As concentration of 150 ppb and pH 4, when the surfactant concentration increased for both surfactants, the removal efficiency increased with low removal efficiencies. Furthermore, efficient removal of As(V) was ensured with the larger MWCO membrane at the 1–3 mM feed CPC concentration (Beolchini *et al.* 2007). From four surfactants (hexadecyltrimethylammonium bromide (CTAB), octadecylamine acetate (ODA), CPC, benzalkonium chloride (BCl)), the lowest removal was exhibited by BCl. The reason for the lower removal of arsenate with BCl was the higher CMC of BCl (5 mM) (Porter 1991). Chen *et al.* (2018) conducted a MEUF experiment using CPC surfactant. They achieved ≥5 mM above the best removal efficiency obtained from the experiments in the range of 0–10 mM CPC concentration.

Impact of initial pH on As-removal

The experimental results of the impact of initial pH on the As-removal efficiency are summarized in Table 5. For 5 mM BCl surfactant, As initial concentration of 500 ppb and pH 4, the removal of As was 37%, which increased to 84% at pH 10. It was the same for the DPClI surfactant, i.e. As-removal at pH 4 was 13.1%, but it increased to 59.4% at pH 10. For both surfactants tested, at 2 mM surfactant and 150 ppb As initial concentrations, an increase in As-removal efficiency occurred with an increase in pH.

Iqbal *et al.* (2007) examined the impact of pH on arsenate removal with the membrane of MWCO 3 kDa. With a decrease in pH to 4, a 2–5% decrease in the removal efficiency occurred because arsenate was present in mono-ionic ($H_2AsO_4^-$) form. The efficiencies at pH 7 and pH 8.5 were determined to be similar due to the di-ionic ($H_2AsO_4^{2-}$) form of arsenate. pH was found to have a similar impact on the arsenic removal in CPC, CTAB, and ODA. Sen *et al.* (2010) also determined that as the pH of groundwater (with 150 g/L arsenic) increased from 3 to 10, an increase in arsenic rejections occurred from 50% to 76% for NF-1, 33% to 69% for NF-2, and 43% to 71% for NF-20 membranes, respectively.

Bahmani *et al.* (2019) investigated the effect of pH on the species of As and reported that as the solution pH increases from 3 to 11, the removal efficiency of As(V) increased from 81.2% to 99.7%. At pH < 6.9, arsenate ions are available in the mono-ionic form, while at pH ≥ 6.9, the di-ionic species of arsenate is dominant. Therefore, at high pH, di-ionic arsenate can bind to more micelles, which resulted in the increased removal efficiency of As(V). As pH increases from 3 to 11, the permeate flux of As(V) decreased from 35.2 L/m^2/h to 3.4 L/m^2/h. In all experiments, pH was set at 7–8 because at this pH the anions were effectively removed.

Impact of membrane MWCO on As-removal

Data on the impact of the As-removal performances of UF membranes having different MWCO values used in the MEUF experiments are summarized in Table 6. An increase in the MWCO of UF membranes resulted in a decrease in As-removal efficiency values for both BCl and DPCl surfactants.

As the pore diameter decreases, the adhesion performance of arsenic on the membrane increases. Similarly, Gecol *et al.* (2004) used CPC surfactant 5 kDA and 10 kDA membranes for the removal of As. The best removal was achieved in the 5 kDA polyethersulphone (PES) membrane.

Table 5 | The impact of initial pH on As-removal

	As (ppb)	Surfactant (mM)	pH	As-removal (%)
BCl	500	5	4	37.0
	500	5	10	84.0
DPCl	500	5	4	13.1
	500	5	10	59.4
BCl	150	2	4	16.6
	150	2	10	60.6
DPCl	150	2	4	16.3
	150	2	10	71.0

Table 6 | The impacts of MWCO on As-removal

BCl	As (ppb)	Surfactant (mM)	pH	As-removal (%)
3 kDa	150	5	10	92.8
10 kDa	150	5	10	71.0
DPCl	**As (ppb)**	**Surfactant (mM)**	**pH**	**As-removal (%)**
3 kDa	150	5	10	63.6
10 kDa	150	5	10	12.1

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Experimental design and response surface modeling of BCl surfactant

It is obvious that the BCl surfactant is more effective than DPCl on the As-removal efficiency in terms of the initial As concentration parameter (Tables 3–6).

According to the experimental design, the results were examined and the removal efficiency of BCl was obtained in Equation (3):

$$\begin{aligned}\mathrm{BCl} = {} & +30.00 - 1.64 * \mathrm{A} + 8.66 * \mathrm{B} + 21.05 * \mathrm{C} \\ & - 2.38 * \mathrm{A} * \mathrm{B} - 2.37 * \mathrm{A} * \mathrm{C} + 3.11 * \mathrm{B} * \mathrm{C} + 2.83 * \mathrm{A2} \\ & + 9.46 * \mathrm{B2} + 7.46 * \mathrm{C2} \end{aligned} \quad (3)$$

subjected to: $-\alpha \leq \mathrm{A},\ \mathrm{B},\ \mathrm{C} \leq +\alpha$; where A, B, and C represent the coded levels of the process variables and α, which is equal to 1.682, represents the 'star' point in the central composite design providing the limits of the valid region.

Student's *t*-test was used for testing the significance of regression coefficients in the response surface equation to the coded variables. The empirical model with actual values is presented below:

$$\begin{aligned}\mathrm{BCl} = {} & +61.956 - 0.006 C_0 - 25.545 S - 5.548\,\mathrm{pH} - 0.009 C_0 S \\ & - 0.004 C_0\,\mathrm{pH} + 0.692 S\mathrm{pH} + 0.00009 C_0^2 + 4.204\, S^2 \\ & + 0.829\,\mathrm{pH}^2 \end{aligned} \quad (4)$$

subjected to: $30 \leq C_0 \leq 620$ (ppb); $0.98 \leq S \leq 6.02$ (w/w); $1.95 \leq \mathrm{pH} \leq 12.05$ where C_0 is the initial As concentration and S is the surfactant concentration.

ANOVA was conducted for testing the adequacy of the regression model, and Table 3 contains the findings on the rejection coefficient.

As a result of assessing the validity of the fitted models for As by ANOVA (Table 7), the findings demonstrate that F-value > F-tabulated and $p < 0.05$. Hence, the regression models were found to be statistically significant at the confidence level of 95% in the examined range. Furthermore, the lack of fit was not significant in any of the presented models at the confidence level of 95% ($p > 0.05$). In As-removal, the response variation percentage that the model explained, R^2, was found to be 0.9653. The adjusted statistic coefficient, R^2_{adj}, was indicated as 0.9030. All the statistical estimators in question indicate that the response model is statistically viable for predicting the response for the range of factors taken into account (valid region). The mentioned results are highly acceptable, and therefore, the model has good validity.

In Figure 1, the impact of pH and surfactant concentration on the As rejection coefficient is illustrated for the initial As concentration of 325 ppb at the center level as a third factor. According to the figure, the lowest As rejection was obtained for pH 1.95 and 3.5 mM surfactant concentration at around 19.3%. The maximum As rejection of 92.8% was acquired at the optimum operating parameters of initial As concentration 150 ppb, pH 10, and 5 mM surfactant concentration.

Jafari *et al.* (2017) evaluated As-removal by employing the MEUF procedure. Furthermore, the RSM and Box–Behnken methods were employed for the purpose of designing the experiments and determining the optimum conditions. The main operational parameters, including pH (4–10), the initial concentration of As (20–80 μg/L), and concentration of CTAB (1–3 mM), were investigated. The removal efficiency obtained was about 94.8% under the optimal conditions (pH = 6.73, initial concentration of arsenic = 29.44 μg/L, and CTAB concentration of 2.83 mM).

Table 7 | ANOVA of the response surface model

Resource	DF[a]	SS[b]	MS[c]	F-value	*P*-value	R^2	R^2_{adj}
Model	10	8,297.5	921.9	15.48	0.0038	0.9653	0.903
Residual	5	297.8	59.6				
Total	15	8,712					

[a]Degree of freedom.
[b]Sum of squares.
[c]Mean square.

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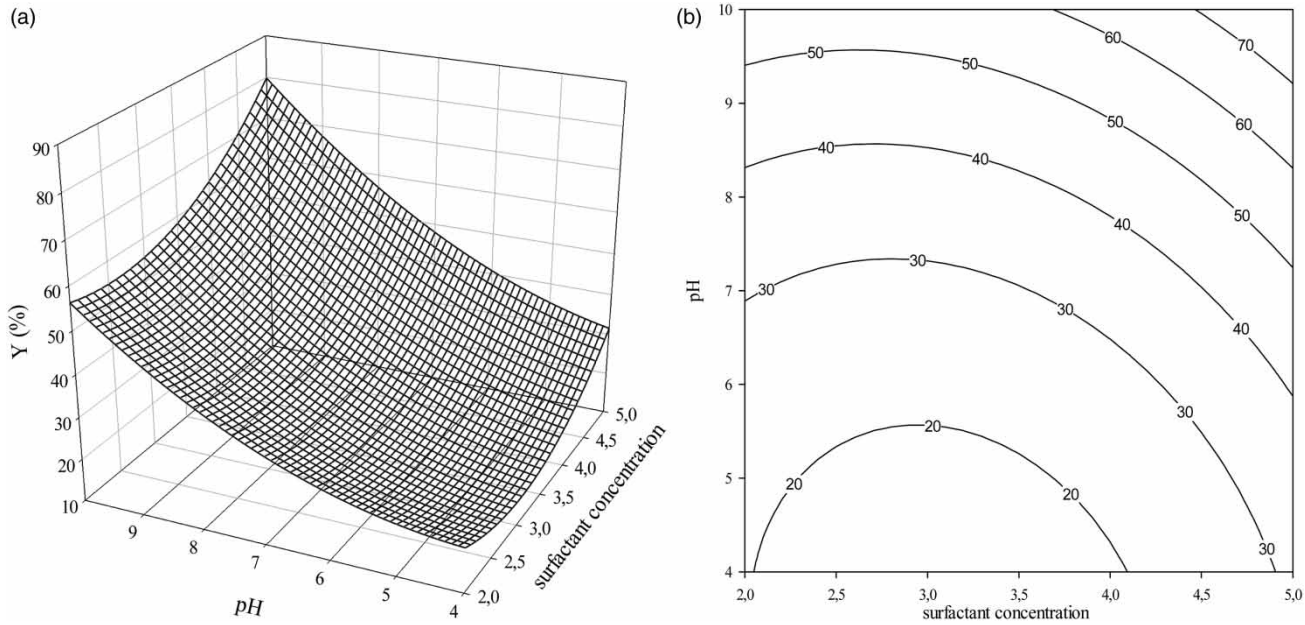

Figure 1 | (a) Response surface plot and (b) contour plots demonstrating the impact of pH and surfactant concentration on the As rejection coefficient for the initial As concentration of 325 ppb.

Figure 2 demonstrates the impacts of two factors, pH and initial As concentration, in various combinations when the third factor was the surfactant concentration of 3.5 mM at the center level. The impact of pH on the As rejection is considerably higher compared to the initial As concentration. As the pH of the solution increased, the rejection efficiency increased and the maximum As rejection was obtained for pH 10. Beolchini *et al.* (2007) investigated

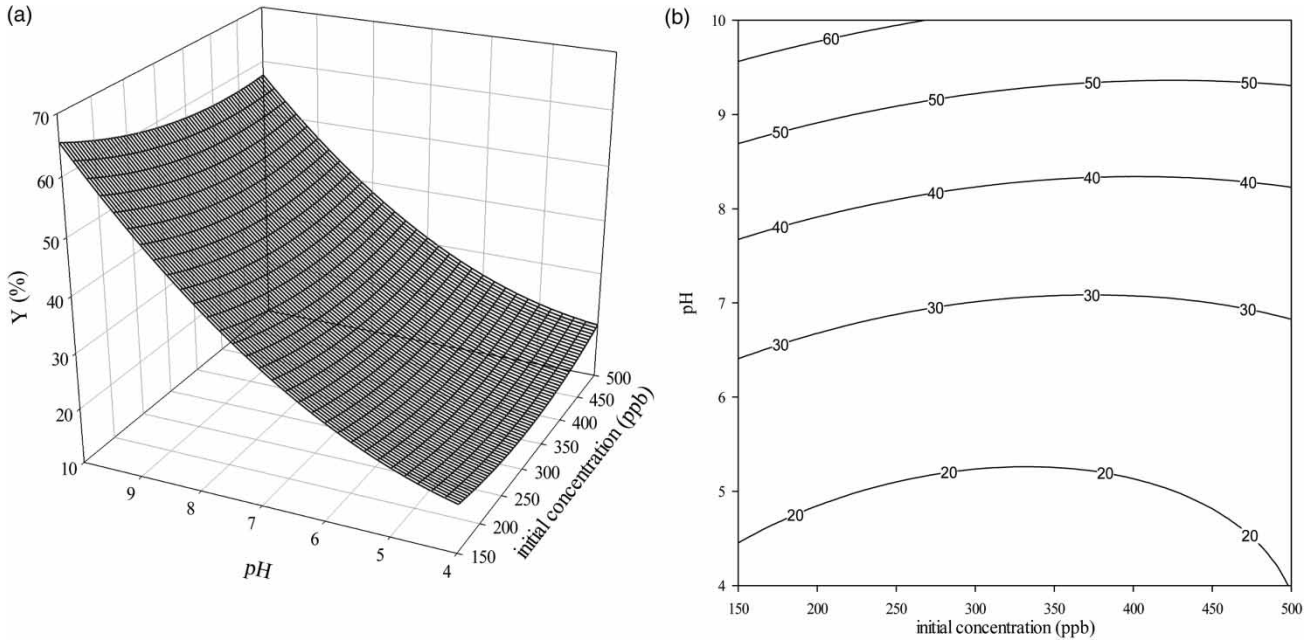

Figure 2 | (a) Response surface plot and (b) contour plots demonstrating the impact of pH and initial As concentration on the As rejection coefficient for the surfactant concentration of 3.5 mM.

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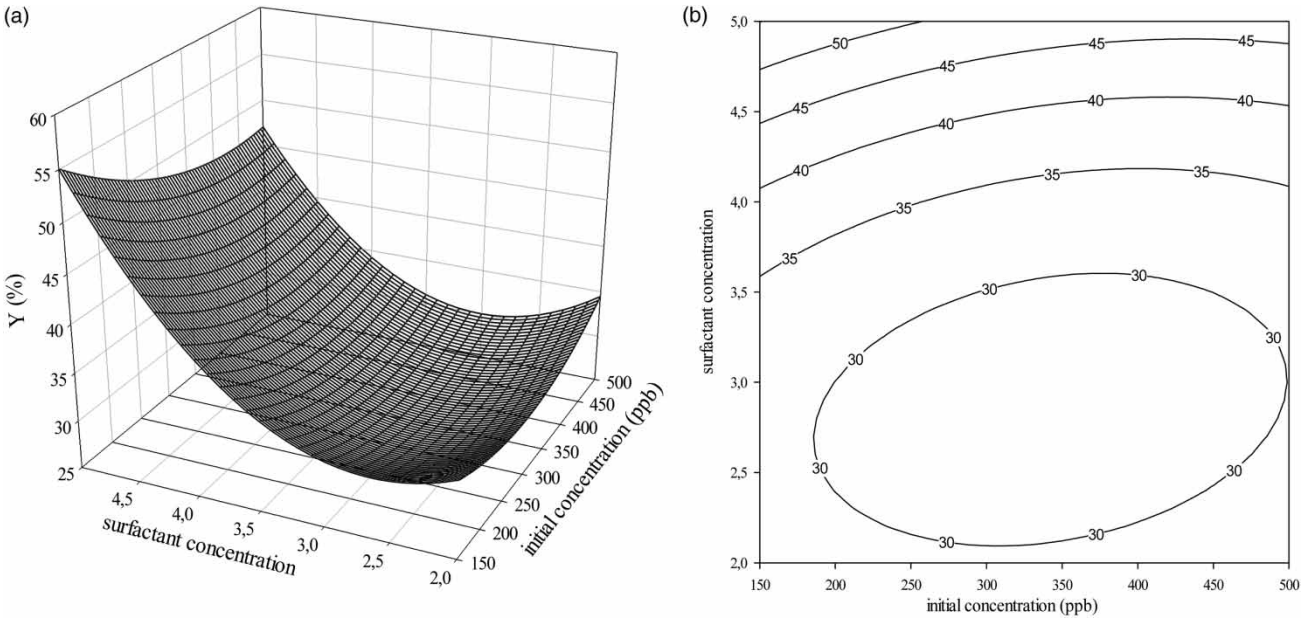

Figure 3 | (a) Response surface plot and (b) contour plots demonstrating the impact of surfactant concentration and initial As concentration on the As rejection coefficient for pH 7.

arsenic removal using CPC and a cross-flow PES membrane. The present research examines the potential benefits of the usage of a large MWCO membrane (100 kDa) and decreased surfactant concentrations (1–3 mM) for the treatment of high fluxes of concentrated arsenic-bearing solutions (6–10 ppm). The PES membrane apparatus with high MWCO ensured the treatment of large fluxes of concentrated arsenic-bearing solutions (6–10 ppm) even with the usage of a low surfactant concentration (1–3 mM). Notably, the removal of arsenic varied between 93–98% and 70–74% based on the initial As concentration (6 and 10 ppm, respectively).

The effects of surfactant concentration and initial As concentration on the As rejection coefficient for pH 7 are shown in Figure 3. Although the increased initial As concentration does not influence the As rejection efficiencies considerably, the increased surfactant concentration leads to an increase in As rejection.

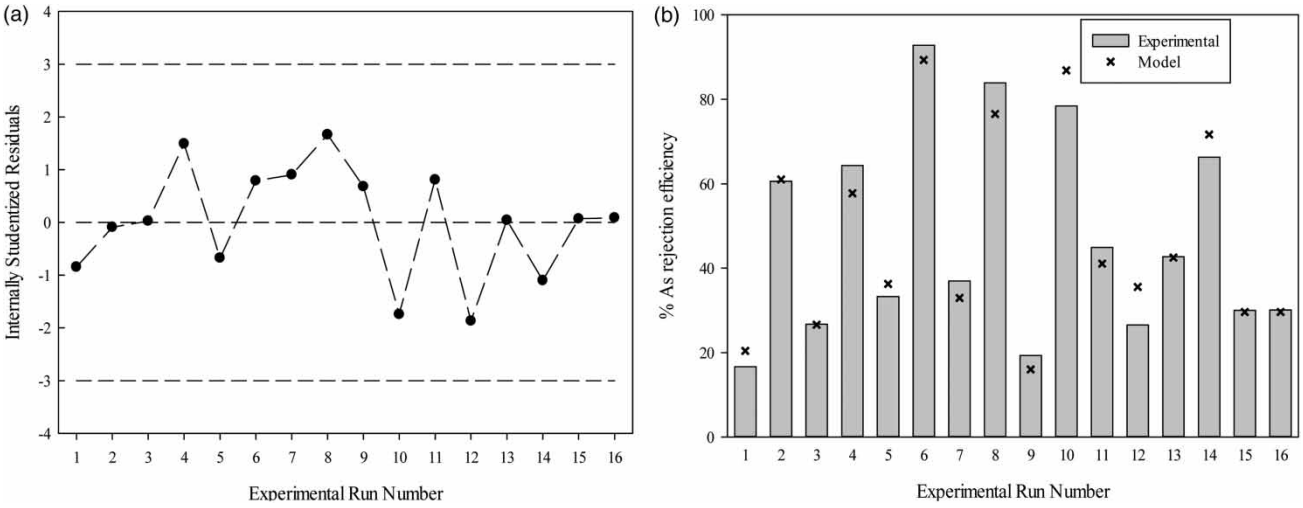

Figure 4 | Experimental data plotted against the response model for the As-removal efficiency (a) and internally studentized residuals (b).

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The experimental data that are plotted against the response model and the internally studentized residuals are given in Figure 4. As is observed, the response surface model exhibits good prediction for the experimental and predicted responses. Studentized residuals were acquired within three sigma limits for the response model and the experimental value, as is wanted.

CONCLUSIONS

The MEUF experiments addressing As-removal from synthetic waters by complexation with BCl and DPCl surfactants were carried out. The experimental results revealed that the pH of the feed solution had a considerable effect on the As rejection efficiency for both surfactants tested. An increase occurred in rejection efficiencies as the pH of the feed solution increased. Furthermore, the impact of the initial concentration of As and surfactant concentration was found to be considerably lower in comparison with the impact of the pH of the feed solution.

The maximum As rejection of 92.8% was obtained for the BCl surfactant at the optimum operating parameters of initial As concentration 150 ppb, pH 10, and 5 mM surfactant concentration. For the BCl surfactant, the operating hydrodynamic conditions were determined in accordance with the full factorial experimental design. ANOVA validated the established response surface models statistically, and they were utilized for the purpose of predicting the removal efficiency over the valid region.

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