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Optimization of micellar enhanced ultrafiltration for arsenic removal from simulated wastewater using experimental and kinetic models

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ABSTRACT

Micellar enhanced ultrafiltration (MEUF) of arsenic-contaminated simulated wastewater was investigated using polyacrylonitrile (PAN) membrane and cetylpyridinium chloride (CPC) surfactant. During experimental studies various operating parameters including, retentate pressure, the molar ratio of CPC to arsenic, initial arsenic concentration, and pH of feed solution were monitored. Ultrafiltration (UF), MEUF, and MEUF in combination with activated carbon fiber (ACF) processes were explored. Multiple linear regression (MLR) model was proposed and its performance was evaluated based on statistical values such as mean square error (MSE), and coefficient of determination (R^2). Moreover, kinetics and isotherm models of MEUF process were studied. The optimum operating parameters were found as retentate pressure of 1.8 bar, surfactant to an arsenic molar ratio of 5:1, initial arsenic concentration 1 mM. Results indicated that arsenic and surfactant removal was 96.13% and 67.48% by MEUF, respectively, while 97.25% arsenic and 98.87% surfactant rejection was achieved through MEUF-ACF whereas, only 37.51% arsenic removal was accomplished by UF. MEUF-ACF process outperformed UF and also shown better results than MEUF. Proposed MLR model presented average results with MSE and R^2 values of 0.68 and 0.74 for testing dataset, respectively. Kinetics and isotherm studies proved that pseudo-second-order equation (R^2 = 0.992) can explain kinetics, while Langmuir isotherm (R^2 = 0.993) was found an appropriate model to depict arsenic adsorption on surfactant micelles.

Keywords: Activated carbon fiber; Arsenic; Micellar enhanced ultrafiltration; Kinetics

1. Introduction

Nowadays, arsenic contamination in waterways has become a global issue, especially in South-East Asia due to its high concentration in water resources, as figures stated that more than 150 million people are affected worldwide from direct or indirect consumption of arsenic-contaminated water [1]. The arsenic polluted water cause diseases like cardiovascular disease, internal malignancies cancers, skin cancer, lungs, bladder and kidney cancer, reproductive disorder, high blood pressure, and paralysis [2–4]. Due to the severity of arsenic associated problems, the maximum contaminant level (MCL) in drinking water had lowered from 50 to 10 ppb in 2001 by the United States Environmental Protection Agency [5]. Therefore, the removal of arsenic pollutants from water streams is necessary to resolve the aforementioned health concerns and to address the environmental issues. There are several conventional techniques generally used to remove arsenic from water sources such as coagulation, precipitation, enhanced coagulation, oxidation, co-precipitation flotation, adsorption, ion exchange, and membrane technology as mentioned in

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previous studies [6–13]. The membrane-based separation is categorized as ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), where UF membranes are superior in terms of higher flux and low energy usage in comparison with NF and RO [6]. Also, surfactant application in combination with UF is known as micellar enhanced ultrafiltration (MEUF) provides collective benefits of RO efficiency and the high flux of UF, which is also an encouraging method to remove substances with lower molecular weight [14–16]. In this method, a surfactant addition up to the critical micelle concentration (CMC) increases the retention coefficient of the pollutants [17].

The previous studies regarding heavy metals removal using MEUF technique [16–19], provided a solid foundation for further research work. A study was performed to analyze the effects of membrane materials, molecular weight cut-off (MWCO), initial arsenic concentration, and pH of the solution on the arsenic removal efficacy and the permeate flux by using cetylpyridinium chloride (CPC). The results presented that polyethersulfone (PES) membranes were found inefficient for arsenic removal without surfactant application while regenerated cellulose (RC) membranes presented better removal efficiency because of their negatively charged surface. By adding 10 mM of CPC to feed water, a reduction in the arsenic concentration of permeate water was noted below the MCL by both PES and RC membranes. Moreover, complete removal of arsenic was attained for 22 and 43 μg/L arsenic concentration of the feed water by using 5 kDa PES and 10 kDa RC membranes at pH values of 5.5 and 8, respectively. For the 5 kDa, PES membrane at a pH of 8, 100% arsenic removal was obtained irrespective of the arsenic concentration in feed water [20]. In another study arsenic removal from groundwater through MEUF by using different cationic surfactants including benzalkonium chloride (BC), hexadecyl pyridinium chloride (HDPC), hexadecyltrimethyl ammonium bromide (CTAB), and octadecylamine acetate (ODA) was explored. The maximum arsenic removal (96%) was achieved in the case of HDPC, 94% using CTAB, with ODA it was above 80% while the BC was least efficient only 57% because of its higher CMC as compared to other surfactants [21]. Also, the consequence of the presence of inorganic solutes on arsenic removal from simulated water and well water through MEUF by using CPC as a surfactant and PES 5kDa ultrafiltration membrane at pH 8 was studied. The dependence of arsenic removal efficiency and permeate flux on the concentration of feed water arsenic and other co-occurring inorganic solutes was noted. It proved that an increase in the concentration of arsenic in the feed water, and the presence of co-occurring inorganic solutes, inversely affect the permeate [22]. The process modeling establishes a relation of operating parameters and removal efficiency of the system to optimize and control the process that is helpful both at designing and operational phases. Artificial neural network (ANN) model was used in MEUF modeling for zinc removal from wastewater that provided promising results [23], response surface methodology was also employed successfully to understand process performance for cadmium and zinc removal [24]. ANN model traced input-output mapping of the MEUF process used for the removal of mercury from simulated wastewater [25] and fuzzy modeling provided satisfactory results to predict the lead removal efficiency of the MEUF process [26]. In our previous study, we optimized the MEUF process for arsenic removal from simulated wastewater using experimental and ANN models where the ANN network presented good prediction results [27].

MEUF process performance is evaluated based on the removal efficiency of both metal and surfactant monomer. Previously, PES and RC membranes were used for arsenic removal from diluted solutions but these studies did not address the secondary pollution caused by leakage of surfactant monomer to permeate water [20,22,28]. Adsorption characteristics that are significant for effective implementation of MEUF for arsenic removal were not studied before as per the author's knowledge although few studies regarding kinetics and isotherm models for other heavy metals adsorption onto the surfactant micelles were conducted [15,29]. Moreover, the application of multiple linear regression (MLR) to optimize MEUF has not been discussed in the previous studies as per our knowledge. The novelty of this work is to evaluate the arsenic removal efficiency of polyacrylonitrile (PAN) membrane for concentrated arsenic-contaminated simulated wastewater for the first time. MEUF in combination with activated carbon fiber (MEUF-ACF) was applied to achieve the highest removal of metal and surfactant as well to address the secondary pollution problem. Optimization of MEUF was studied experimentally by considering various operating parameters one by one including retentate pressure, CPC to arsenic molar ratio, initial arsenic concentration, and pH of the feed solution. Adsorption characteristics of arsenic ions on CPC micelles were studied by employing kinetics and isotherm adsorption models. Moreover, the MLR model was proposed by considering, time, retentate pressure, the molar ratio of CPC to arsenic, initial arsenic concentration, and pH of the feed solution as independent variables while arsenic removal efficiency was the only dependent variable.

2. Materials and methods

2.1. Materials

Sodium arsenate ($Na_2HAsO_4·7H_2O$) with a purity of 99% was purchased from Junsei Chemicals, Japan. The cationic surfactant was CPC with 98% purity was procured from Daejung Chemicals & Metals, South Korea with 98% purity. The chemicals used to adjust pH of feed solution and in the cleaning process including, sodium hydroxide beads with assay above 97% and hydrochloric acid with purity above 35% were also obtained from Daejung Chemicals & Metals, South Korea. PAN-based UF membrane characteristics are presented in Table 1, were procured from Synopex Membrane Filter, South Korea, and five-micron cartridge filters were also obtained from the same supplier. ACF made of carbon impregnated pleated polyester was purchased from 3M Company, China. The deionized water was used during experiments, including solutions preparation and cleaning process. The experimental setup of MEUF-ACF is depicted in Fig. 1, which comprises a feed and cleaning tank, ultrafiltration membrane, permeate, and permeate storage tanks. UF is a cross-flow type filtration where the rejected solution is recirculated into the feed tank, whereas, permeate water is collected separately [15,18,30]. The feed pump is used to pump feed water through the UF membrane during operation and cleaning pump for cleaning of the UF membrane by providing flow in the reverse direction. As shown in Fig. 1, ACF unit consists of a five-micron cartridge filter (CF) used before ACF to prolong their life and to maximize CPC removal from the MEUF effluent [16].

2.2. Methods and analysis

The glassware used in the experimentation was cleaned with regular laboratory detergent and rinsed with deionized water. $Na_2HAsO_4·7H_2O$ and CPC were, respectively, used as sources of arsenic and surfactant to prepare feed solution. The solutions were prepared by mixing stoichiometric amounts of arsenic and CPC surfactant in 3 L of deionized water and kept shaking at 100 rpm for an hour. For each run of experiments, fresh solutions were prepared to avoid any interference. The pH of the solution without any adjustment was measured as 8.3 by using Multifunction meter CX-505, Elmetron, Poland, and then pH of the solution was set according to tested values in this study. The tested experimental parameters are summarized in Table 2. The cleaning of the UF membrane was performed by using deionized water followed by 0.1 M NaOH solution, and reflushing with deionized water. Similarly, cleaning of the membrane was performed with 0.5% HCl and flushed with distilled water. Moreover, CF and ACF were cleaned with deionized water first and then soaked in 0.1 M of NaOH and 2% of HCl for a day. Lastly, washed them with distilled water to prepare for the next run of experiments [15,16]. CPC concentration in the simulated wastewater, permeate and retentate water samples were measured using UV/VIS-3600Plus (Shimadzu Corporation, Japan) spectrophotometer at a wavelength of 258 nm. Freshly prepared standard

Table 1
Characteristics of UF membrane

Membrane material	Polyacrylonitrile
Membrane type	Hollow fiber
Flow direction	Inside to outside
Flow type	Cross-flow
Effective surface area, m^2	0.055
Membrane diameter (inside/outside) mm	0.8/1.4
Molecular weight cut-off (MWCO)	10 kDa

Table 2
MEUF experimental operating parameters

Operating parameters	Tested values
Retentate pressure (bar)	1.5, 1.8, 2.2, 2.5
Molar ratio of CPC to arsenic (mM)	3:1, 5:1, 8:1, 10:1
Initial arsenic concentration, (mM)	1, 1.5, 2, 3
pH	7, 7.5, 8, 8.5
Sampling time (min)	10, 20, 30, 40, 50, 60

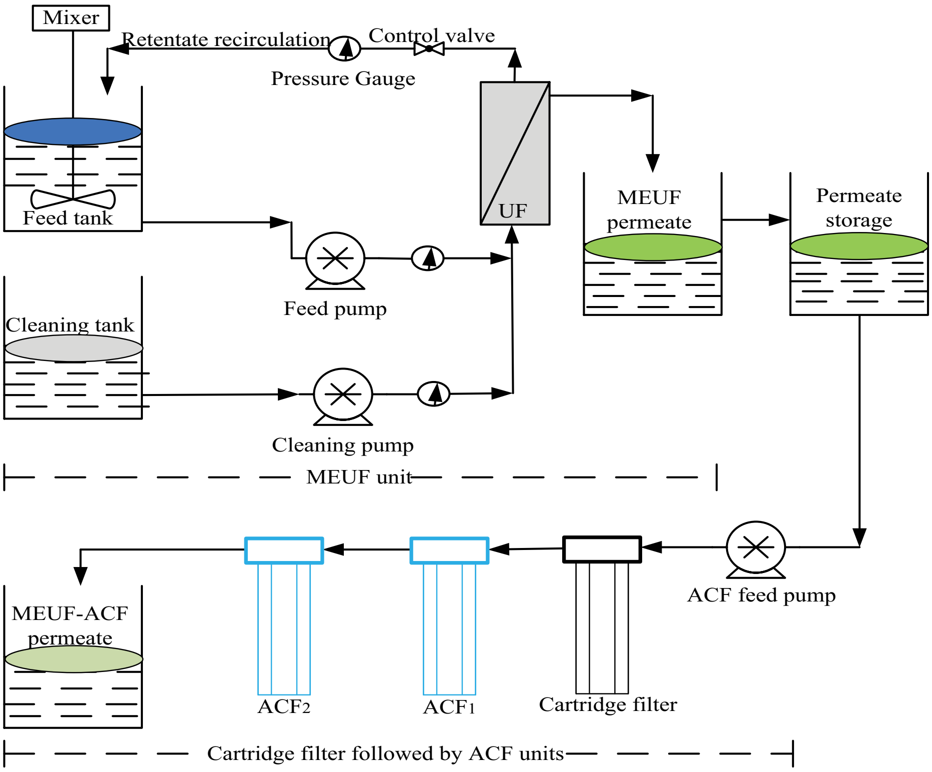

Fig. 1. MEUF-ACF experimental setup.

solutions of CPC and blank samples (DDI water) were used for spectrophotometer calibration. Arsenic concentration in simulated wastewater, permeate, and retentate water samples were determined by using inductively coupled plasma-optical emission spectrometry ICP-OES technique (720-ES, Varian), US EPA Method 6010 [31,32]. The standard calibration solutions containing arsenic were prepared from a stock solution at predefined concentrations of 0.2, 1, 5, and 10 ppm. Before arsenic analysis feed water samples were diluted as required. A maximum temperature of 400°C was maintained in a chamber containing a glass nebulizer with a nebulizer gas flow of 0.75 L/min. The flow rate of water samples introduced to the apparatus was 0.5 L/min and axial analysis was done at a 15 mm view distance. Plasma and auxiliary gas flows were maintained at 15 and 1.5 L/min, respectively, using argon gas. Initially, instrumental calibration was monitored using arsenic standard calibration solutions concentration as mentioned above. The test results were checked by observing the arsenic concentration of standard quality control solutions and noted that results were within the limits. The duplicate samples were prepared and analyzed to confirm the results. The removal percentage of arsenic and CPC was calculated using Eq. (1).

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{1}$$

In this Eq. (1), R represents rejection (%), C_p is the permeate concentration, while C_f is the feed solution concentration.

2.3. MLR model

MLR model is a statistical technique used to predict the relationship between two or more independent variables and a dependent variable by fitting a linear equation to experimental data. In this model, once the relationship between independent and dependent variables has been learned by model then it can predict the dependent variable with an unseen dataset that can be checked with an experimental dataset to justify the model results. The coefficient of determination (R^2) is a statistical metric used to measure the performance of the model [33]. A simple mathematical relation used in the calculation shown in Eq. (2).

$$Y = \beta_0 + \beta_1 X_1 + \ldots + \beta_n X_n + \varepsilon \tag{2}$$

In this Eq. (2), Y denotes a dependent variable, X_i denotes independent variables, β_i denotes predicted parameters and ε is the error term [34]. In this study MLR technique chosen to develop a relationship between MEUF metal removal efficiency as a dependent variable while five independent variables were selected as independent variables such as time, retentate pressure, the concentration of feed solution, molar ratio of surfactant to metal, and pH of feed solution. In this work Python programming (3.7) was used where a built-in pandas library is available for MLR, therefore, no theoretical equation was required to develop the MLR model. The statistical information of the dataset is presented in Table 3. In this model, an experimental dataset was divided randomly into training (80%) and testing (20%) of a dataset. After training the proposed MLR model, it was tested with the unseen dataset (testing dataset) and results were compiled. MLR model was proposed by using Python programming, a soft computing technique with a random data split into 80% for training and 20% for testing. The performance of the model for the testing dataset was measured by statistical metrics as described in the following section. In Python programming (3.7) using the pandas' library, a linear regression model was imported from the sklearn.

2.4. Model predicted results evaluation

The aim of model performance evaluation is to confirm the accuracy of the proposed model to check any error for its application with confidence [35,36]. In this study, two performance criteria were used to check the proposed model predicted results. Mean square error (MSE) Eq. (3) and coefficient of determination (R^2), Eq. (4) were used as performance measuring criteria in the evaluation of the model as described below.

$$\text{MSE} = \left[\frac{1}{n}\left(\sum_{i=1}^{n}\left(Y_{\text{exp}}^{i} - X_{\text{pre}}^{i}\right)^2\right)\right] \tag{3}$$

$$R^2 = \left[\frac{n\sum_{i=1}^{n} y_{\text{exp},i}\, y_{\text{pre},i} - \left(\sum_{i=1}^{n} y_{\text{exp},i}\right)\left(\sum_{i=1}^{n} y_{\text{pre},i}\right)}{\sqrt{\left[n\sum_{i=1}^{n} y_{\text{exp},i}^2 - \left(\sum_{i=1}^{n} y_{\text{exp},i}\right)^2\right] \times \left[n\sum_{i=1}^{n} y_{\text{pre},i}^2 - \left(\sum_{i=1}^{n} y_{\text{pre},i}\right)^2\right]}}\right]^2 \tag{4}$$

2.5. Adsorption kinetic studies of MEUF

The kinetic studies have the utmost importance to understand the mechanism, equilibrium conditions, and the rate constant for adsorption of adsorbate onto the adsorbent. The kinetic studies of a process provide an important understanding of the reaction pathway [37]. This kinetic study of MEUF presented the adsorption ranges of CPC micelles and arsenic during 10–60 min filtration at CPC and arsenic concentration of 5 and 1 mM respectively. Arsenic ions were adsorbed by the CPC micelles which acted as an adsorbent in this system. An assumption was made that CPC micelles were totally removed by UF and arsenic ions were adsorbed by CPC micelles excluding the ions that pass into permeate as mentioned in previous studies [29,38]. The adsorbed amount of arsenic per unit mass of CPC micelles known as adsorption capacity (mg/g) was calculated by using Eq. (5) [38].

$$G = \frac{C_{f,M} \times Q_f - C_{p,M} \times Q_p}{C_{f,\text{CPC}} \times Q_f - C_{p,\text{CPC}} \times Q_p} \tag{5}$$

where G represents the adsorption capacity (mg/g), $C_{f,M}$ and $C_{p,M}$ are concentrations of arsenic in feed and permeate (mg/L), respectively, $C_{f,\text{CPC}}$ and $C_{p,\text{CPC}}$ are concentrations of CPC in feed and permeate (g/L), respectively, and feed and permeate fluxes are denoted by Q_f and Q_p (L/m² h), respectively. The rate constants of arsenic ions adsorption on CPC micelles for various adsorption range in terms of arsenic concentration were computed by using linearized kinetic models as reported by Huang et al. [38], Krishnan et al. [39], and Ho et al. [40]. Calculations and data analysis was conducted by using Tableau Desktop Professional Edition software and MS-Excel professional 2019.

2.6. MEUF adsorption isotherm studies

The adsorption isotherm studies of MEUF were performed at laboratory temperature 20°C ± 1°C, with 5 mM concentration of CPC and arsenic concentration varied from 1 to 3 mM. In this study, two prominent isotherm models, including Langmuir and Freundlich were used to explore the experimental data. The Langmuir isotherm model considers monolayer coverage, energetically equivalent surface sites, and adsorbing ability at a specific site of a molecule to be independent of surrounding sites and has successful applications in actual adsorption process and can be expressed as presented by [41,42]. A non-linear regression study was conducted using Tableau professional software to find the parameters of the model. The Freundlich isotherm is frequently used for heterogeneous surface energy systems and evaluated as described by Freundlich [43].

3. Results and discussion

Each operating parameter was investigated one by one while others were kept constant. In the following section, results are presented concerning arsenic and CPC removal using UF, MEUF, and MEUF-ACF processes, prediction results of MLR model, kinetics, and isotherm models investigation also described in next sections given below.

3.1. Effect of retentate pressure on arsenic removal

Analysis of the initial retentate pressure on arsenic removal was performed at defined values as presented in Table 2. Fig. 2 demonstrates that average arsenic removal was 92.87%, 96.13%, 97.01%, and 97.20% at retentate pressure of 1.5, 1.8, 2.2, and 2.5 bar, respectively, at molar ratio 5:1 of CPC to arsenic, the arsenic concentration of 1 mM without any pH adjustment. Similar trends of pressure effect were presented for other heavy metals such as chromate, nickel, and cadmium removal from aqueous solution [15,16,18]. At high pressure the gel layer thickness increased on the membrane surface and ultimately increases the removal of metal micelle complex. The concentration polarization occurs due to the increase of pressure that generates a concentrated layer of surfactant monomer near to the membrane surface causing additional resistance and also increase osmotic pressure [28]. Therefore, optimum pressure is a significant parameter in the MEUF process that was observed as 1.8 bar for maximum arsenic removal with best permeate flux at a molar ratio of 5:1 without doing any adjustment of pH.

3.2. Effect of molar ratio of CPC to arsenic on arsenic removal

Multiple experiments were conducted to analyze the effect of CPC to arsenic molar ratio at the aforementioned fixed retentate pressure and permeate flux. As presented in Fig. 3 average removal of arsenic was 99.00%, 98.15%, and 96.51% for a molar ratio of 10:1, 8:1, and 5:1, respectively, keeping retentate pressure at 1.8 bar and arsenic concentration of 1 mM without any pH adjustment. An improvement in arsenic removal was noted corresponding to an increase in CPC to arsenic molar ratio. This improvement occurred due to more micelles formation at higher CPC concentration, which increases the available micelle

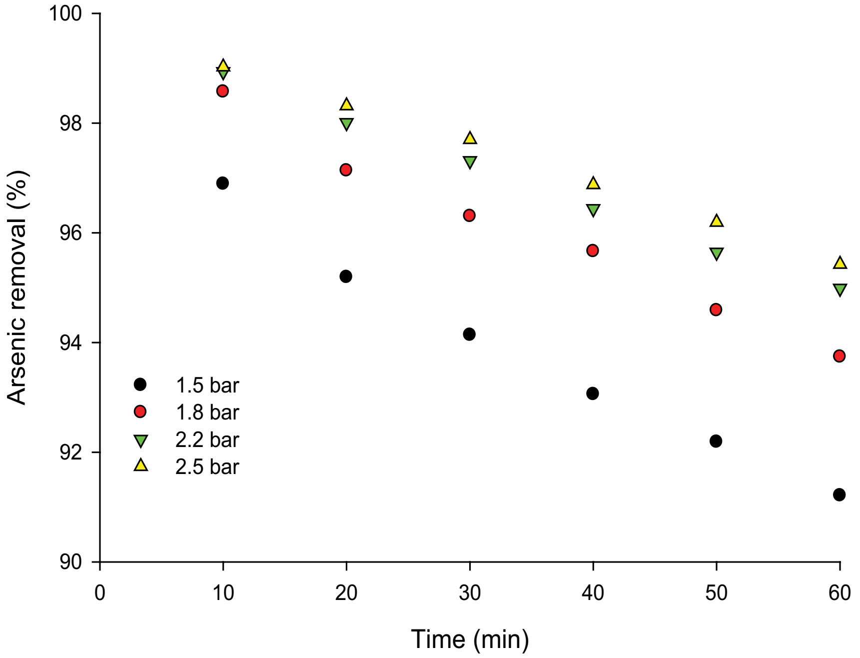

Fig. 2. Effect of retentate pressure on arsenic removal.

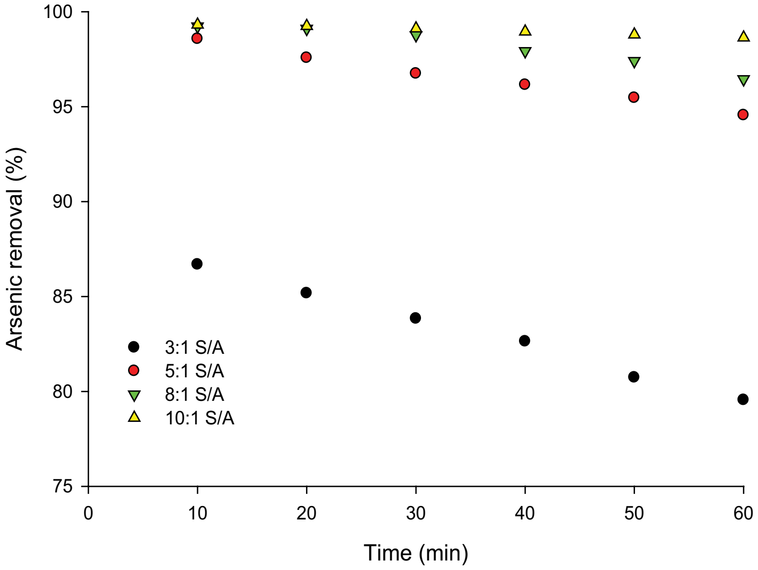

Fig. 3. Effect of molar ratio of CPC to arsenic on arsenic removal.

Table 3
Data statistics of model variables ($n = 96$)

Variables	Data statistics			
	X_{min}	X_{max}	X_{mean}	σ
Independent variables				
Time (min)	10.00	60.00	35.00	17.08
Pressure (bar)	1.50	2.50	1.85	0.209
Arsenic concentration (mM)	1.00	3.00	1.219	0.529
Molar ratio	3.00	10.00	5.375	1.495
pH	7.00	8.50	7.938	0.299
Dependent variable				
Removal efficiency	55.913	100	91.79391	9.835

X_{min}, X_{max}, X_{mean}: minimum, maximum, and mean values; σ: standard deviation.

surface area for attracting arsenic ions electrostatically. Previously done studies supported these results [16,18,28]. The optimum molar ratio of CPC to arsenic was noted as 5:1 that provides 96.13% average removal of arsenic at 1.8 bar retentate pressure.

3.3. Effect of initial arsenic concentration on arsenic removal

A series of experiments were performed with different initial arsenic concentrations of feed solution such as 1, 1.5, 2, and 3 mM while CPC to arsenic molar ratio was 5:1 and 1.8 bar retentate pressure at room temperature without any pH adjustment. The average arsenic removal efficiency was 96.13% for 1 mM concentration of arsenic while 87.25%, 74.55%, and 67.80% arsenic rejection were found for an initial arsenic concentration of 1.5, 2, and 3 mM, respectively, as presented in Fig. 4. Arsenic removal decreases with increasing initial arsenic concentration as studied by Gecol et al. [20] and Beolchini et al. [28] and a similar trend for other heavy metals including cadmium, chromium, and nickel was presented in the literature [15,16,18]. This suggests that the concentration of arsenic in permeate water increased proportionally to initial concentration of arsenic in feed water due to the availability of lesser micelle surface area to adsorb higher metal concentrations electrostatically, that is, the higher initial concentration, the lower removal efficiency. As a result of an increase in metal concentration available surface for metal ions adsorption becomes insufficient so excess ions remained soluble in the solution and ultimately drop the removal efficiency [44]. The 1 mM arsenic concentration of feed solution was found optimum as it provides higher removal efficiency of arsenic 96.13% while other parameters were kept constant.

3.4. Effect of pH on arsenic removal

A number of experiments were conducted to explore the effect of various pH values including 7.0, 7.5, 8.0, and 8.5 on arsenic removal from simulated wastewater by keeping retentate pressure 1.8 bar, molar ratio of CPC to arsenic 5:1, and feed solution arsenic concentration of 1 mM. It was observed that arsenic removal was slightly increased by changing pH from 7 to 8 (94%–96%) as shown in Fig. 5, but above pH value of 8.0 no increase in arsenic removal efficiency was observed. This result is supported by a study that presented improvement in the arsenic removal efficiency of the MEUF process by increasing pH from 5.5 to 8 [20]. In addition, it was reported that As(V) species were found neutral at pH 1.0 while between pH 2.22 and 6.98, they change from neutral to mono-anionic form. Further, at a pH value of 6.98, mono-anionic to di-anionic dissociation happened. Hence, maximum arsenic removal takes place at a pH value of 8, due to the likely binding of di-anionic arsenate to the micelles [20]. Literature studies presented that the removal of arsenic is proportional to the pH value of the feed solution. Therefore, in the acidic environment,

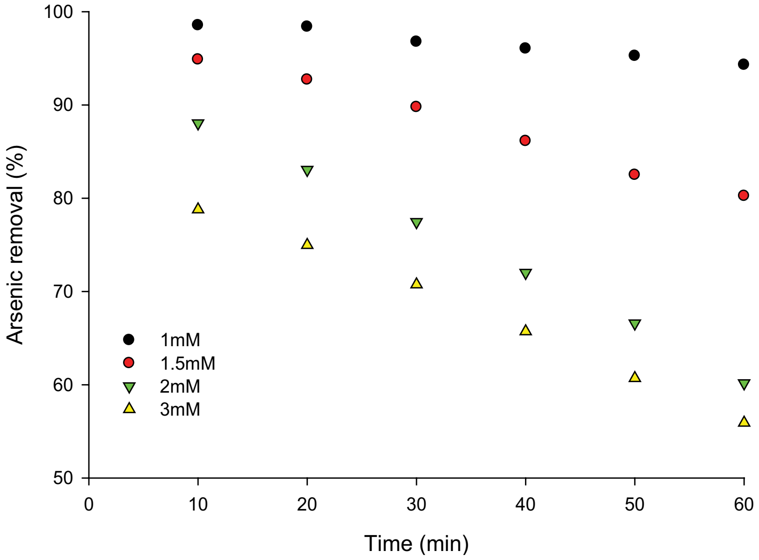

Fig. 4. Effect of arsenic concentration on arsenic removal.

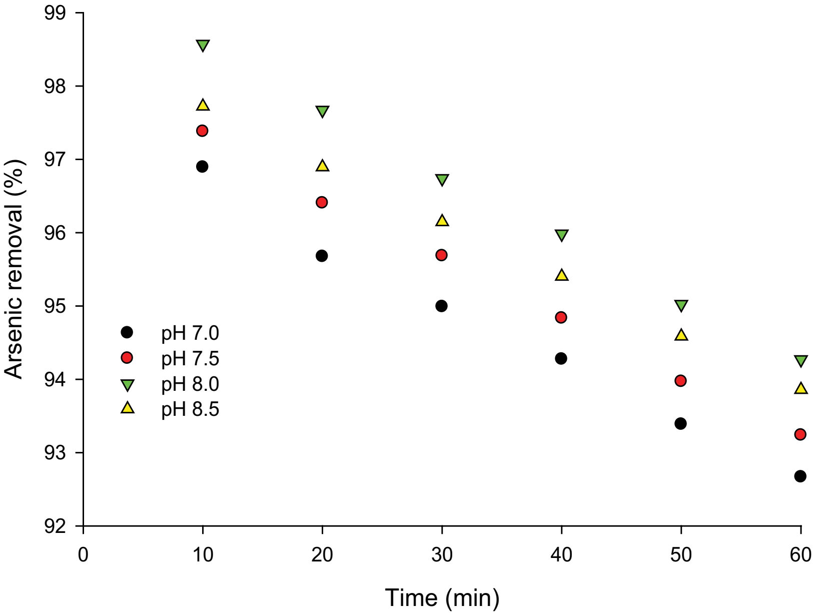

Fig. 5. Effect of pH on arsenic removal.

adsorption of arsenic onto the micelle surface was decreased that ultimately reduces arsenic removal efficiency from simulated wastewater while at high pH value di-ionic species of arsenate can bind to more micelles that cause higher removal efficiency of arsenic as presented in another recent study [45].

3.5. Comparative study of UF, MEUF, and MEUF-ACF techniques

For ultrafiltration (UF) set of experiments was performed for 1 mM of arsenic concentration without CPC addition. The average arsenic removal was 37.45% within a 1 h operation and the trend of removal % with respect to time is shown in Fig. 6. The results indicated that only UF cannot remove arsenic due to the smaller size of metal ions than the pore size of the membrane. The removal was only because of adsorption onto the membrane surface and inside the pore walls [16]. The rejection was low at the start but with the passage of time due to film formation on membrane surface retention improved. However, a small increase in retention was observed after 40 min of filtration. In UF no significant decrease in permeate flux was observed because there was no accumulation of micelles on the membrane surface. Moreover, experiments were repeated at similar conditions applied in UF but 5 mM of CPC concentration was added to form micelles to enhance arsenic removal efficiency. The results presented that MEUF performed much

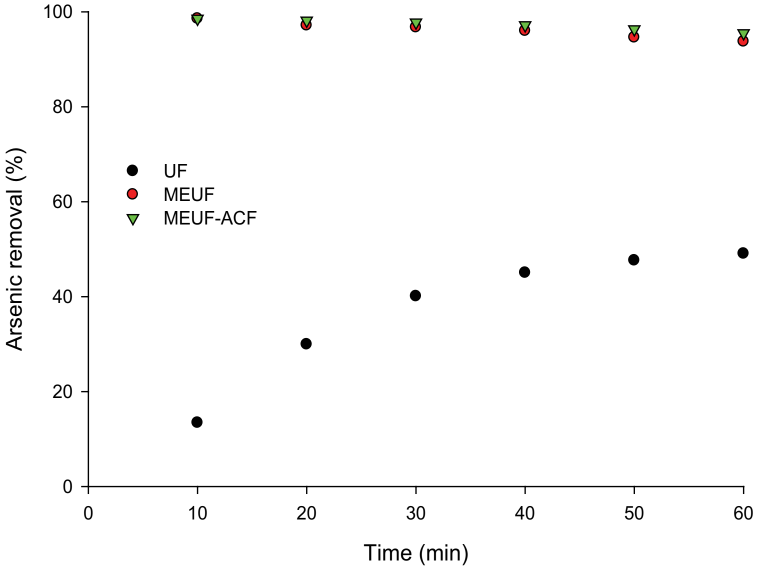

Fig. 6. Arsenic removal by UF, MEUF, and MEUF-ACF.

better than UF because of micelles formation in the solution that easily retained by the UF membrane as 96.13% and 67.48% of arsenic and CPC was removed, respectively during MEUF process. Furthermore, a set of experiments was performed to explore the removal of excess arsenic ions and surfactant monomers present in the MEUF permeate by connecting with the ACF unit. It was observed that arsenic removal was slightly increased (97.25%) using MEUF-ACF technique as presented in Fig. 7 while CPC removal was increased to 98.87%. The CPC concentration in MEUF permeate was less than CMC while it was below the detection limit in the permeate of MEUF-ACF. The experimental results proved that MEUF-ACF may be a promising technique for arsenic and CPC removal from wastewater. In this hybrid technique, a drawback of MEUF, secondary pollution caused by the leakage of surfactant monomers to the permeate was addressed. A comparative study at optimum operating parameters shown that arsenic removal was 37.15% in UF, arsenic, and CPC removal was observed as 96.13% and 67.48% in MEUF, respectively, while maximum removal of arsenic and CPC was achieved 97.25% and 98.87%, respectively in MEUF-ACF.

3.6. MLR model results

The proposed MLR model was assessed by comparing its predicted results with experimental results indicated an average distribution around the $X = Y$ line with an

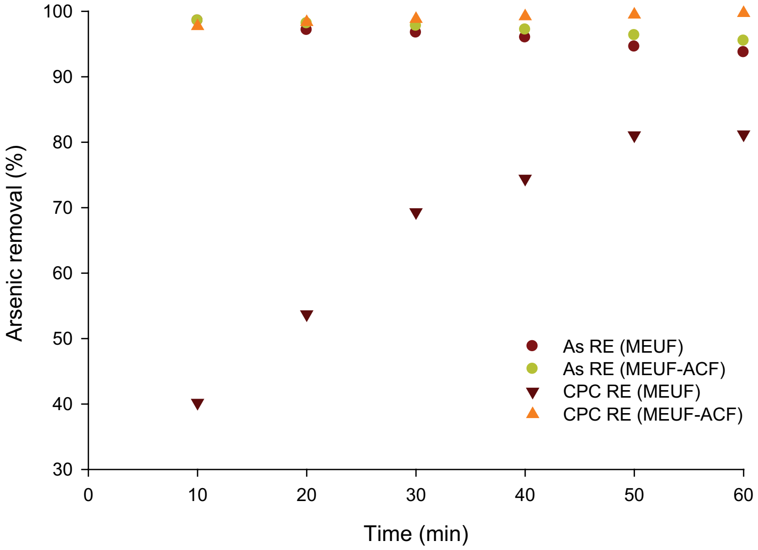

Fig. 7. Arsenic and CPC removal by MEUF and MEUF-ACF.

average MSE value of 0.68 and R^2 = 0.74 as presented in Fig. 8. This result confirms the MLR model is not as successful as the ANN model for the prediction of metal removal efficiency of the MEUF process. As reported in the literature ANN model provided promising results in the modeling of the MEUF process for the removal of zinc [23], mercury [25], and arsenic from the simulated wastewater [27]. In addition fuzzy modeling provided satisfactory results to predict the lead removal efficiency of the MEUF process [26] and response surface methodology also presented good results to understand MEUF process performance for cadmium and zinc removal [24]. In this study, MLR model was proposed and its prediction results were not promising as compared to previous studies that indicate arsenic removal efficiency of MEUF process has not a linear relationship with operating parameters including, time, retentate pressure, initial concentration of feed solution, the molar ratio of surfactant to arsenic, and pH of the feed solution. The proposed model can be used to compare its results with other models predictions to find the most suitable model for other heavy metals to optimize the MEUF process and to prove the type of relationship between operating parameters and removal efficiency of the process. Therefore, the MLR model cannot be a good alternative to the experimental work for MEUF process optimization to predict arsenic removal efficiency as compared to other modeling techniques.

3.7. Kinetics studies analysis

The kinetic fitting curves for arsenic ions adsorption onto CPC micelles are shown in Fig. 9 (a) first-order kinetics, (b) pseudo-first-order kinetics, (c) second-order-kinetics, and (d) pseudo-second-order kinetics. The adsorption kinetic equations are presented in Table 4 with a value of rate constant and correlation coefficient. The first three of the aforementioned kinetic models such as (a) first-order-kinetics, (b) pseudo-first-order kinetics, and (c) second-order-kinetics yielded R^2 values of 0.823, 0.823, and 0.8986, respectively. It means that first-order and pseudo-second-order kinetics provided a lesser degree of fit from the experimental dataset with R^2 value of 0.823 by drawing a linear plot of t against $\ln(G - G_e)$ and $\log(G - G_e)$, respectively. This indicates that after a specific time interval the quantity of bound arsenic onto the surfactant micelles reached a saturation point. So, these kinetic models cannot be suggested as a demonstrative model because of their validity over a limited period and considerable change in equilibrium adsorption values occurred [46]. As second-order-kinetics describes that the sorption rate is higher at the start of a process but slows down as equilibrium state approaches. To figure out the importance of chemisorption experimental results were tested with second-order-kinetics that provided better results (R^2 = 0.8986) as compared to first-order and pseudo-first-order kinetics but these kinetic models were considered inadequate to characterize arsenic CPC micelles interactions. In this study, the pseudo-second-order kinetic model (R^2 = 0.992) was found an appropriate kinetic model to explain arsenic ions adsorption on CPC micelles. The pseudo-second-order model is based on the assumption that chemisorption might be a rate-limiting step in the process. Therefore, it can be concluded that the adsorption of arsenic on to the surfactant micelles is governed by the chemisorption process. It is evident from correlation coefficients values that pseudo-second-order kinetic model fits well as previous studies have reported similar results of arsenic adsorption on various adsorbents [47–49] as chromium adsorption is presented [46]. It indicates that the pseudo-second-order kinetic model followed chemisorption as a rate-limiting step in arsenic CPC micelles interactions throughout adsorption phenomena.

3.8. Analysis of isotherm studies

The adsorption capacity (G) was calculated according to Eq. (5) and then the adsorption isotherms parameters were determined using Tableau Desktop Professional Edition software and MS-Excel professional 2019. The adsorption of arsenic ions on CPC micelles is shown in Fig. 10, (a) Langmuir isotherm and (b) Freundlich isotherm

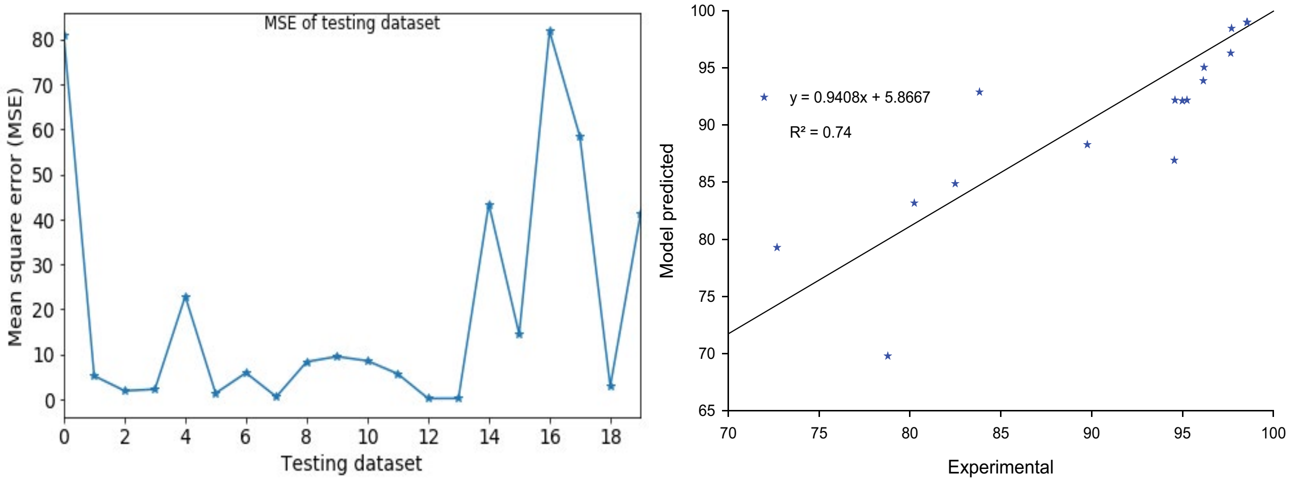

Fig. 8. MLR model performance evaluation (MSE and R^2) of testing dataset.

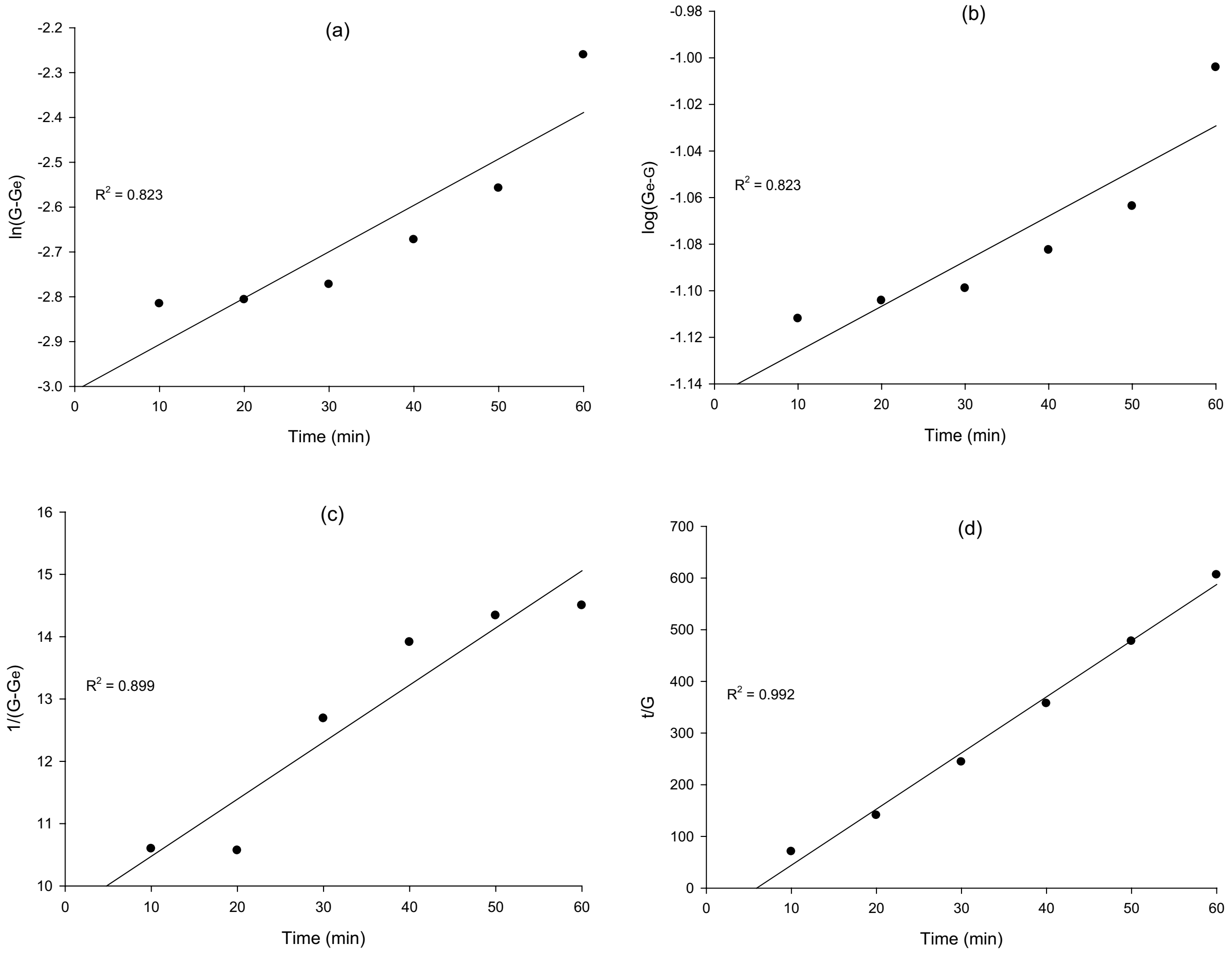

Fig. 9. Adsorption kinetics fitting curve for arsenic ions adsorption on CPC micelles: (a) first-order-kinetics, (b) pseudo-first-order kinetics, (c) second-order-kinetics, and (d) pseudo-second-order kinetics.

Table 4
Adsorption kinetic equations including rate constants and correlation coefficient R^2 values

Kinetics models	Kinetic equations	Rate constant	R^2
First-order	$\ln(G - G_e) = 0.0103t - 3.0098$	–0.0103 (K_{ad}, 1/min)	0.823
Pseudo-first-order	$\log(G_e - G) = -0.0019t - 1.009$	–0.0044 (K_1, 1/min)	0.823
Second-order	$1/(G - G_e) = 0.0916t + 9.559$	0.0916 (K_2, g/mg min)	0.899
Pseudo-second-order	$t/G = 10.86t - 64.094$	10.86 (K_2^*, g/mg min)	0.992

model. These adsorption isotherm models and their respective equations are presented in Table 5. Since the values of correlation coefficient (R^2) for Langmuir isotherm at optimum operational conditions of MEUF process such as retentate pressure of 1.8 bar, CPC to the arsenic molar ratio of 5:1, initial arsenic concentration 1 mM and pH 8 for arsenic-contaminated simulated wastewater treatment is very close to 1, thus monolayer adsorption is attained and the process becomes highly promising. The results showed that the Langmuir isotherm model ($R^2 = 0.993$) was more suitable to explain arsenic CPC micelles interactions as compared to the Freundlich isotherm model ($R^2 = 0.923$). Langmuir isotherm model indicates surface homogeneity of adsorbent, and basic consideration of this model is also based on monolayer coverage of adsorbate on adsorbent's surface. Arsenic adsorption on CPC micelles can be described much better through homogenous adsorption rather than heterogeneous adsorption. Langmuir isotherm can be tested by comparing the theoretical adsorption calculations made by Langmuir adsorption isotherm with experimentally obtained results that show strong compatibility between the experimental and calculated values having the highest correlation. There are no studies regarding arsenic adsorption on CPC micelles but a detailed study of

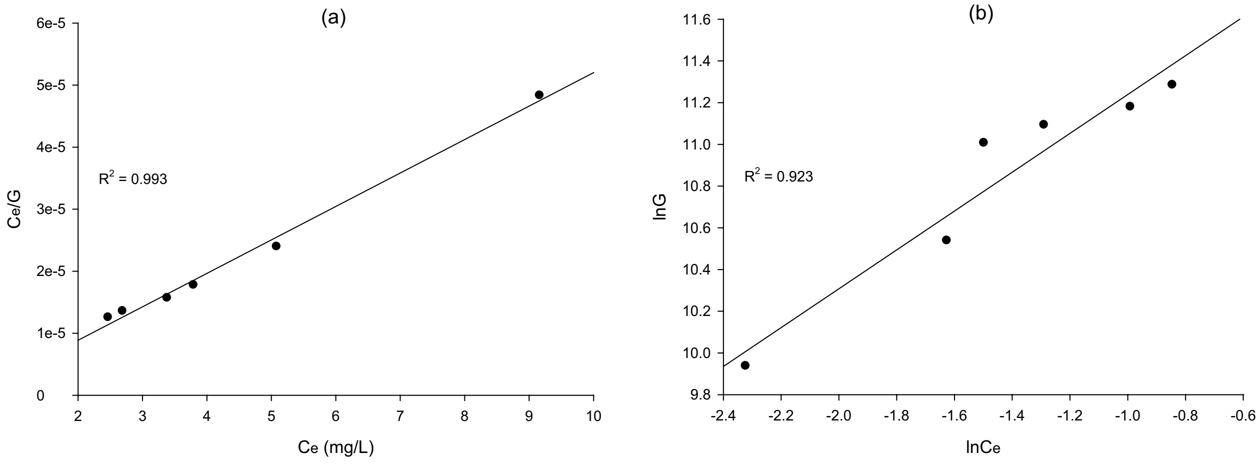

Fig. 10. Adsorption isotherm fitting curves for arsenic ions adsorption on CPC micelles: (a) Langmuir isotherm and (b) Freundlich isotherm.

Table 5
Adsorption isotherm models along with equations and correlation coefficient R^2 values

Isotherm models	Isotherm equations	R^2
Langmuir	$C_e/G = -5.0 \times 10^{-5} C_e - 2.0 \times 10^{-6}$	0.993
Freundlich	$\ln G = 0.9906 \ln C_e - 12.167$	0.923

arsenate adsorption onto iron hydroxide presented similar results [47].

4. Conclusion

Optimization of the MEUF process for arsenic removal from simulated wastewater was conducted through experimental and MLR model by considering various operating parameters including, retentate pressure, CPC to arsenic molar ratio, initial arsenic concentration, and pH of feed solution. UF was also performed for comparative studies while MEUF-ACF was employed to address the secondary pollution. Moreover, kinetics and isotherm models of the MEUF process were explored to find the best model for adsorption of arsenic on to the surfactant micelles. The optimum operating parameters were found experimentally as retentate pressure of 1.8 bar, CPC to the arsenic molar ratio of 5:1, initial arsenic concentration 1 mM. A comparative study presented average arsenic removal of 37.51%, 96.13%, and 97.25% for UF, MEUF, and MEUF-ACF, respectively. The surfactant rejection by MEUF and MEUF-ACF process was noted as 67.48% and 98.87%, respectively. Hence, MEUF-ACF may be a promising technique for arsenic and surfactant removal from wastewater. The proposed MLR model demonstrated average results when compared with experimental results having MSE of 0.68 and R^2 of 0.74. Therefore, the MLR model cannot be a good option to predict heavy metals removal efficiency of the MEUF process. The adsorption kinetics and isotherm studies showed that pseudo-second-order kinetic equation (R^2 = 0.992) can explain kinetics, while Langmuir isotherm model (R^2 = 0.993) was found suitable to depict arsenic adsorption on to the CPC micelles.

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