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Optimization of arsenite removal by adsorption onto organically modified montmorillonite clay: Experimental & theoretical approaches

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Abstract−Arsenic is a critical contaminant for aqueous environments as it poses harmful health risks. To meet the stringent regulations regarding the presence of arsenic in aqueous solutions, the feasibility of montmorillonite clay modified with hexadecyltrimethyl ammonium chloride as the adsorbent was tested for the removal of arsenic ions from aqueous solutions. A scanning electron microscopy (SEM) study confirmed that the organically modified nanoclay (ONC) adsorbent had a porous structure with a vast adsorbent surface. The x-ray fluorescence (XRF) analysis proved the presence of carbon in the structure of the modified nanoclay that can be evidence for the creation of ONC. The x-ray diffraction (XRD) analysis results confirm the existence of four main groups of minerals, carbonate (Calcite), clay (Askmtyt and Kandyt), silicate (Quartz), and phyllosilicate (Kaolinite), in the ONC structure.The influence of various parameters such as solution pH, adsorbent dosage, initial arsenite concentration, and contact time on arsenic adsorption onto ONC was investigated. A 2^5 full factorial central composite experimental design was applied. A central composite design under response surface methodology (RSM) was employed to investigate the effects of independent variables on arsenite removal and to determine the optimum condition. The experimental values were in a good fit with the ones predicted by the model. The optimal operating points (adsorbent dosage: 3.7 g L^{-1}, surfactant dosage: 3 g L^{-1} and the contact time: 37.2 min) giving maximum arsenite removal (95.95%) were found using Solver "Add-ins" in Microsoft Excel 2010.

Keywords: Modeling, Response Surface Methodology, Organic Nanoclay, Arsenite, Optimization

INTRODUCTION

Arsenic predominantly exists in aqueous solutions in inorganic forms such as arsenite (As (III)) and arsenate (As(V)) [1]. These forms are classified as carcinogenic and can enter aqueous systems by leaching from soils and minerals [2]. They lead to a wide range of problems from skin pigmentation disorders to nervous disorders andcancer [4]. The hazardous health effects of arsenic on humans, animals, and plants has caused increasing global concerns [4-8]. International reports indicate that a 3 μg/L concentration of arsenic can lead to bladder and lung cancer that causes between 4 and 7 deaths per 10,000 people [9,10]. Additionally, there are reports that indicate that this figure increases up to 23 deaths per 10,000 people with arsenic amounts of 10 μg/L [11]. In most countries, the maximum contaminant level (MCL) in drinking water has been set to 50 μg/L [5,10]; however, the MCL has been lowered in many

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places, as the World Health Organization (WHO) recommended an MCL of 10 μg/L in 1993 [11]. Furthermore, the US Environmental Protection Agency (EPA) has recommended a lower standard of 5 μg/L [8]. Arsenic has been removed from water solutions by chemical precipitation and membrane and adsorption processes [12-16]. These methods have different advantages and disadvantages [17-19]. Chemical precipitation produces sludge containing large amounts of toxic arsenic, while the disadvantage for membrane technologies include high cost [20,21]. Adsorption is a quick and easy method with smaller sludge production and no production of harmful secondary products [22]. Although, activated carbon is widely used in wastewater treatment systems [23,24], naturally abundant clay minerals (e.g. montmorillonite) are regarded as good adsorbents.This is due to their unique properties such as high ion-exchange capacity, swelling property, micro and meso-porosity and also their surface properties [25]. Clay materials have dimensions in the nanometer range. They may be regarded as nano-material with geological and pedological origins [26,27]. Clay materials are usually characterized by features like having a layered structure with a dimension in the nano scale, where the thickness of the 2 : 1 layer is about 0.7 nm. Because of high water absorption by clay, and the infeasibility of separation of heavy metals, the surface properties of clay minerals can be changed by replacing the exchangeable inter-layer cations with organic cationic surfactants, as the nature of the surface can be altered from hydrophilic to hydrophobic [28,29]. Organic surfactants are usually used to create organophilic (hydrophobic) surfaces in clay materials. The present study was conducted by cation exchange between hexadecyltrimethyl ammonium chloride (HDTMA-Cl) as the surfactant and the clay, which is known as intercalation [27]. Organically modified nanoclaysare widely used as adsorbents for the removal of organic pollutants and metal ions. The suitability of these organically modified nanoclays as adsorbent can be because of their nano-size and specific surface area and also their great tendency to absorb ions and organic compounds [30]. Therefore, organically modified nanoclays may be suitable for the removal of organic and inorganic pollutants from wastewater. This research was conducted to optimize arsenite adsorption onto ONC using response surface methodology (RSM). Optimization using the classical method (by changing one factor and fixing others) is not as precise and reliable as expected, because it does not depict the interactive effects between all the factors involved. Also, these studies necessitate spending considerable time and doing numerous tests. Henc RSM may be considered an efficient way to deal with the limitations of the conventional method. The main objective of RSM is to determine the optimum operational conditions for the system that can result in improved product yields, reduced process variability, closer correspondence of the output response to nominal and target requirements, and also reduced development time and overall costs [27,31,32].

EXPERIMENTS

1. Preparation and Characterization of ONC

Nanoclay (brand cloisite Na$^+$) was purchased from Gonzales, Texas, USA Co. The mineral type of the nanoclay was montmorillonite. HDTMA-Cl was used as a surfactant to modify the nanoclay particles. Cation exchange capacity (CEC) was used to prepare different concentrations of the surfactant. For this purpose, 1 g nanoclay was exposed to 100 mL of arsenite solution (10 mg L^{-1}). Then the sample was filtered and measured. It was found that CEC is 0.36 (meq As/g nanoclay). Different concentrations of 0.94, 1.63, 2.31 and 3 mMol/L of HDTMA-Cl were added to the Erlenmeyer flasks (250 mL). Then, 3 g of nanoclay was added to each of the flasks. The samples were stirred for 24 hours on a shaker (20 °C, 300 rpm and pH 7.0) and then were centrifuged. The final product was first washed several times with deionized water and then dried in an oven at 105 °C. Thus, four types of ONC were prepared. Finally, the prepared adsorbents were kept inside sealed polyethylene bottles. The schematic of the ONC is shown in Fig. 1. The value of 3 mMol/L of the HDTMA-Cl surfactant was selected for the characterization of ONC. The morphology of nanoclay, before and after modification, was ascertained with scanning electron microscopy (SEM) analysis (Hitachi S-3000N, Japan). The chemical composition of the adsorbent, before and after modification, was determined by x-ray fluorescence (XRF) spectroscopy (Shimadzu XRF-1800 with Rh radiation). The powder x-ray diffraction (PXRD) patterns of the ONC were collected using a Philips-Magix Pro MPD (PANalytical 3040/60 X' Pert PRO) with a high

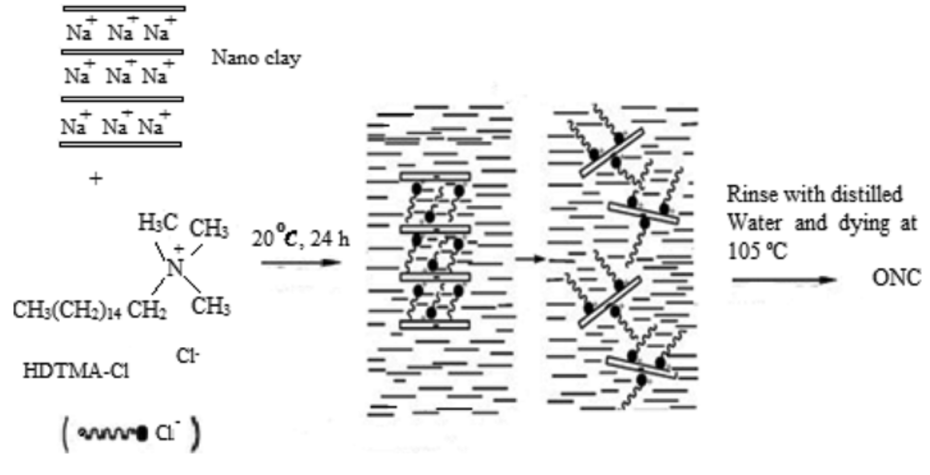

Fig. 1. Schematic representation of the modified organic nano-clay for the preparation of ONC nanocomposites.

power Cu Kα radioactive source over a range of 0-120 at a scan speed of 1 s/step, 1.54 Å wavelength and 25 °C. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis was employed to accurately measure the total area of the porous samples and calculate the distribution of pore size, respectively.

2. Analysis and Adsorption Experiment

An arsenite stock solution (1 mg As cm^{-3}) was prepared by dissolving 1 g sodium (meta) arsenite $NaAsO_2$ (Sigma-Aldrich, 99%) in double distilled water. Then, the desired As (III) concentrations were obtained by the dilution of the stock solution.The adsorption experiments were conducted according to the RSM method. All the experiments were carried out using several 250 mL Erlenmeyer flasks containing 100 mL of arsenite solution at the desired concentrations. The initial pH of the solution was adjusted at the desired level and the required dosage of the adsorbent was added in the flask. Solutions were mixed for a predetermined time period. After the passage of the specified time, samples were centrifuged to separate the adsorbent (5,000 rpm). The residual concentration of arsenic was analyzed using atomic absorption spectrometry.

3. Experimental Design

RSM was applied by using a central composite design (CCD) as a statistical experimental technique for predicting and modeling the complicated relations between input-independent factors (pH (x_1), adsorbent dose (x_2), initial arsenic concentration (x_3), surfactant dose (x_4) and time (x_5)) and one dependent output response (arsenite removal efficiency (Υ)). The actual values of the independent variables that were used for the experimental designare given in Table 1. A full factor design (considering the five above-mentioned controllable variables) was designed using the R software for Windows (version 3.0.3:6 March 2014) to determine the true range of factors, and also their effects on arsenite removal. Totally, 47 runs were designed using a 2^5 full factorial (the base design), 6 axial points and 9 replicates in the center point. The coded values of the independent variables were calculated based on Eq. (1):

$$x_i = \frac{(X_i - X_0)}{(\Delta X)} \qquad (1)$$

where X_i is a coded value of the independent variable, X_0 is the center point value, and ΔX is the change value. A quadratic model as Eq. (2) was used to express the interaction between (Υ) and (x_1, x_2, x_3, x_4 and x_5):

$$\Upsilon = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k-1}\sum_{j=1}^{k} b_{ij} X_i X_j + C \qquad (2)$$

where b_0 is the intercept value, b_i, b_{ii}, and b_{ij} refer to the regression coefficient for linear, second order, and interactive effects respectively, x_i and x_j are the independent variables, and C denotes the error of prediction [33-35].

Table 1. Real and coded values of independent variables used for experimental design

Variable	Symbol	Coded level		
		−1	0	1
		Real values		
pH	X_1	3	7	11
Adsorbent dose (g L^{-1})	X_2	1	3	5
Initial arsenic concentration (mg L^{-1})	X_3	1	2.5	4
Surfactant dose (g L^{-1})	X_4	0.94	1.97	3
Time (min)	X_5	5	32.5	60

RESULTS AND DISCUSSION

1. Characterization of the Sorbent

The SEM micrographs of the nanoclay and ONC samples are shown in Fig. 2(a)-(b). While the overall morphology of the nanoclay and ONC was similar, a porous structure with vast adsorbent surface was observed for ONC, which can be attributed to the 24 h treatment (formodification) and may be responsible for the higher capacity of adsorption. The XRD patterns of ONC are displayed in Fig. 3. The XRD analysis confirmed the mineralogical composition of the samples. ONC appears to have the characteristic peaks of the four main groups (carbonate (Calcite), clay (Askmtyt and Kandyt), silicate (Quartz), and phyllosilicate (Kaolinite) and also the sub-groups (Muscovite, Illite, Calcite and Poligourcite)). Gypsum has also been observed in some analyzed samples. The chemical compositions and characteristics of the nanoclay and ONC adsorbents were determined by the XRF instrument and are summarized in Table 2. Based on the results, the main composi-

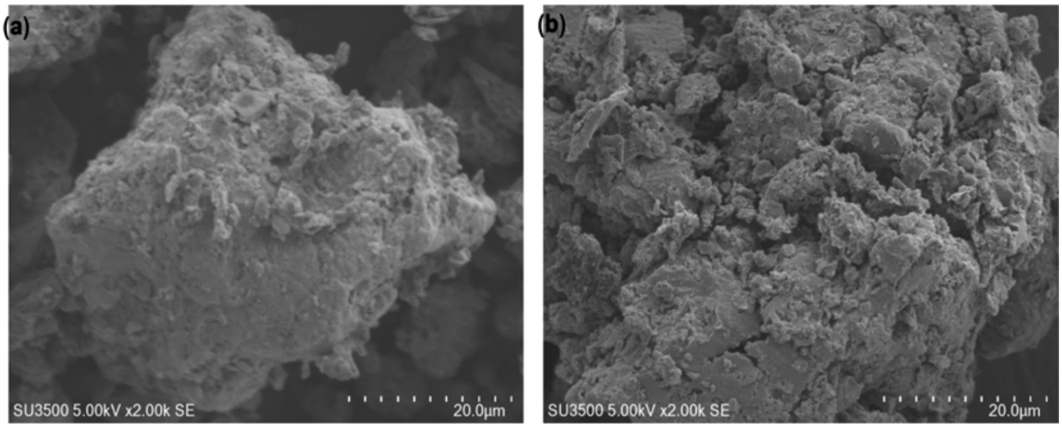

Fig. 2. SEM images of nano-clay (a) and modified nano-clay (b).

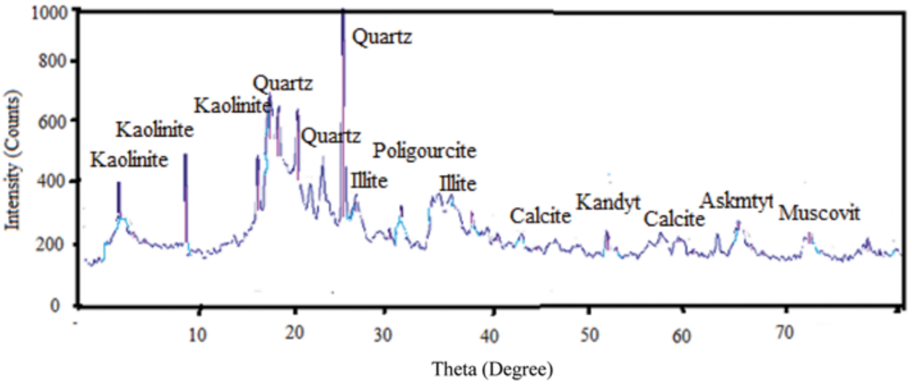

Fig. 3. The XRD analysis for determination of the minerals in organic nano-clay.

Table 2. XRF analysis for determination of element compounds of contained in the nano-clay and ONC

Constituent	Percent	
	Nano-clay	ONC
C	-	42.31
TiO_2	-	0.23
V_2O_5	-	0.05
Au	7.89	-
Al_2O_3	22.11	18.29
CaO	1.9	-
K_2O	0.98	-
MgO	2.45	2.04
SiO_2	42.47	20.01
Na_2O	4.16	2.98
Fe_2O_3	8.19	5.14
Co	-	0.08
Cl^-	-	2.77

tion of the nanoclay and ONC consists of SiO_2 and carbon, respectively, in which the presence of carbon in the structure of modified nanoclay can be evidence for the creation of ONC. Amounts of all elements decreased in ONC in comparison with nanoclay. The BET analysis results showed that the total specific surface area=4.46 m^2/g and the total pore volume=0.0068114 cm^3/g for the nanoclay that compared with the total specific surface area=61.99 m^2/g and the total pore volume=0.11 cm^3/g for ONC. The BJH analysis was employed to determine the particle size of the sample, and the results are shown in Fig. 4. The BJH analysis showed a mean pore diameter of 6.1 nm and 7.5 nm for the nanoclay and ONC, respectively.

2. Main Study

To study the combined effects of variables on arsenicremoval efficiency, statistically designed adsorption experiments were performed at the specified combinations of the physical parameters. Showing the levels of variables, the experimental and the predicted data for the removal of arsenite by ONC in the CCD experimental design are presented in Table 3. It has been stated that, in the RSM method, the identification of the optimum conditions of operation is not possible [29,34] and an optimization process is needed to obtain the results presented in Table 3. From Table 3, arsenite removal efficiencies for different conditions lie between 21.1% (run 16) and 92.8% (run 40). The lowest arsenite removal efficiency was related to runs numbers 8, 9, 10, 15, 16 and 29. The pH and initial arsenic concentrations had no significant effects on arsenic adsorption onto ONC (run numbers of 16, 38 and 40), while changing the adsorbent, surfactant and time levels resulted in increased adsorption efficiency by ONC (run numbers of 24 and 40). The

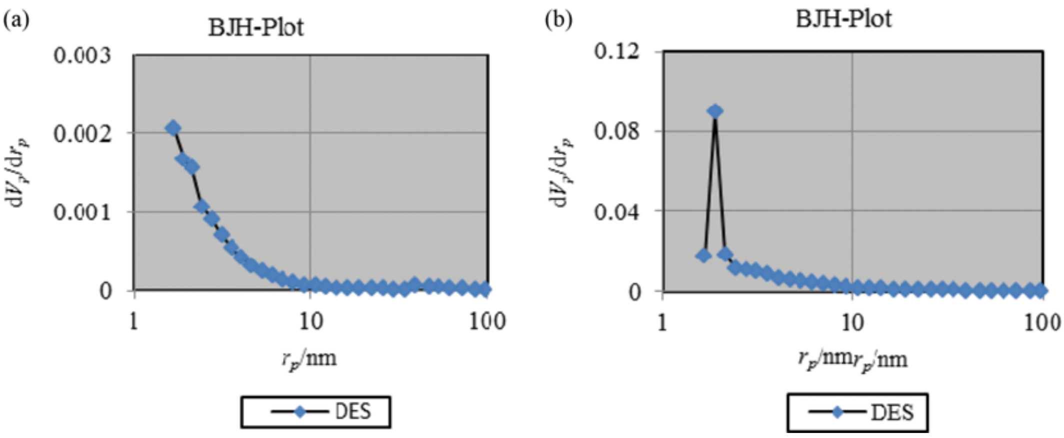

Fig. 4. Determination of the distribution of particle size (a) nano clay (b) ONC.

Table 3. CCD experimental design for arsenic removal by organic nano clay

Run	X_1	X_2	X_3	X_4	X_5	Expt.	Pred.	Run	X_1	X_2	X_3	X_4	X_5	Expt.	Pred.
1	5	2	2	2.31	18.75	72.2	72	25	7	3	3	1.63	32.5	85.43	74.7
2	5	4	4	0.94	18.75	47.2	49	26	9	4	4	2.31	18.75	82.44	80.6
3	9	2	2	0.94	18.75	41.21	40.39	27	5	4	2	0.94	18.75	52.24	49.01
4	5	4	4	2.31	18.75	78.34	80.62	28	7	3	3	1.63	32.5	85.43	74.7
5	9	4	4	2.31	46.25	88.44	90.36	29	5	2	2	0.94	18.75	40.3	40.4
6	7	3	3	1.63	60	62.99	61.06	30	7	3	3	1.63	32.5	85.43	74.8
7	9	2	2	2.31	46.25	87.18	81.7	31	9	2	4	2.31	46.25	85.4	81.7
8	7	1	3	1.63	32.5	58.4	66.1	32	9	2	2	2.31	18.75	78.2	72
9	9	4	2	0.94	46.25	54.4	58.7	33	5	4	2	2.31	46.25	87.78	90.3
10	5	2	4	0.94	18.75	34.63	40.39	34	5	4	2	2.31	18.75	78.71	80.62
11	5	2	2	2.31	46.25	85.2	81.7	35	3	3	3	1.63	32.5	60.4	74.7
12	7	3	1	1.63	32.5	79.54	74.7	36	11	3	3	1.63	32.5	82.1	74.7
13	7	3	3	1.63	32.5	63.4	74.7	37	5	4	4	0.94	46.25	65.87	58.7
14	7	5	3	1.63	32.5	81.4	83.4	38	5	4	4	2.31	46.25	88.1	90.36
15	7	2	3	1.63	5	31.5	37.28	39	9	2	2	0.94	46.25	58.22	50.1
16	7	2	3	0.25	18.75	21.1	14.09	40	9	4	2	2.31	46.25	92.8	90.36
17	5	2	4	2.31	18.75	67.2	72	41	9	4	2	2.31	18.75	84.22	80.62
18	9	2	4	2.31	18.75	81.45	72	42	9	4	4	0.94	18.75	57.78	49.01
19	5	4	2	0.94	46.25	67.1	58.7	43	9	4	4	0.94	46.25	60.14	58.7
20	9	2	4	0.94	46.25	60.94	50.1	44	5	2	2	0.94	46.25	50.49	50.1
21	9	4	2	0.94	18.75	55.27	49	45	7	3	5	1.63	32.5	77.1	74.78
22	7	3	3	1.63	32.5	85.43	74	46	9	2	4	0.94	18.25	47.1	39.8
23	5	2	4	2.31	46.25	83.17	81.7	47	5	2	4	0.94	46.25	54.7	50.1
24	9	3	3	3	32.5	91.31	92.6								

removal efficiency decreased dramatically when these terms were combined, e.g., run number 16 [29,36,37]. By direct reading of the RSM Table, run number 40 was chosen as the optimum condition, as it showed the highest removal efficiency. Although, some runs (such as run numbers 5 and 24) can be considered as eligible conditions, but required surfactant dosage in them was higher than run number 40, which is vital for economical feasibility. The conditions for run number 40 were: a pH of 9.0, an adsorbent dosage of 4.0 g L^{-1}, an initial arsenite concentration of 2 mg L^{-1}, a surfactant dosage of 2.31 g L^{-1} and the time of 46.25 min.

3. The Development of the Regression Model Equation and the Analysis of Variance

The reduced quadratic model was generated by multiple regression, and summarized in Table 4. According to Table 4, it is obvious that the adsorbent dosage (x_2), the surfactant dosage (x_4) and the time (x_5) (p-values<0.05) have a significant impact on the response prediction by the model, while pH (x_1) and initial arsenic concentration (x_3) (p-values>0.05) have shown the opposite effect.This can be evident for results presented in the previous section. Therefore, the x_1 and x_3 terms were removed from the model and the reduced quadratic model is presented with (x_2), (x_4) and (x_5) terms. According to the obtained results, all the present terms in Table 4 are significant (p-values<0.05); therefore, all terms could be entered into the model formula. This shows that x_2, x_4 and x_5 have a synergistic effect on the response prediction by the model, while (x_4^2) and (x_5^2) have an antagonistic effect on the model. The obtained equations from the quadratic model, for both coded and uncoded values of the parameters, are presented at Eqs. (3) and (4), respectively. These models can be used for prediction and optimization [33-35,38].

$$\Upsilon=83.52+8.09\ X_2+18.48\ X_4+10.84\ X_5-8.14\ X_4^2-23.45\ X_5^2 \tag{3}$$

$$\Upsilon=-39.3+4.31\ X_2+46.8\ X_4+2.37\ X_5-7.3\ X_4^2-0.03\ X_5^2 \tag{4}$$

Table 4. Regression analysis for the reduced quadratic model

Model term	Coefficient estimate	Std. error	t-Value	p-Value
(Intercept)	−39.3	13.44	−2.93	0.005627
x_2	4.31	1.457	2.96	0.005077
x_4	46.8	11.807	3.69	0.000289
x_5	2.37	0.589	4.029	0.000237
x_4^2	−7.3	3.575	−2.067	0.045128
x_5^2	−0.03	0.008	−3.399	0.001517

Analysis of variance (ANOVA) can be used to demonstrate model adequacy [34,35,38]. ANOVA is a statistical technique that subdivides total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [34,35,37,39]. The results of ANOVA are summarized in Table 5. According to the ANOVA, a higher 'F' statistic value of 16.46 indicates that most of the variation in the response can be explained by the regression equation. In addition, a lower 'P' value (<0.01) and a higher R^2 value (0.8) indi-

Table 5. Analysis of variance (ANOVA) for the reduced quadratic model

Model formula in RSM (X_2, X_4, X_5)	DF	Sum of squares	Mean square	F-value	Probability (P)
First-order response	3	11778.8	3926.3	43.9698	2.781×10^{-12}
Pure quadratic response	3	1367.0	455.7	5.1030	0.004686
Residuals	37	3303.9	89.3	-	-
Lack of fit	6	748.7	124.8	1.5138	0.206413
Pure error	31	2555.2	82.4	-	-

Notes: Multiple R-squared: 0.8001, Adjusted R-squared: 0.7815, F-statistic: 16.46 on 9 and 37 DF, p-value: 1.937×10^{-10}

cate that the second-order polynomial model is an adequate modelfor representing the actual relationship between the response and variables; thus, the model fitted experimental results well [38,40]. This implies that more than 80% of the data deviation can be explained by the independent variables; however, data deviation should not be assessed only by this parameter (R^2). The adjusted R-squared value (0.78) of the model is very close to the multiple R-squared value, representing a satisfactory agreement between the quadratic model and the experimental data [39-41]. The multiple R-squared value should be close to the adjusted R-squared value. The multiple R-squaredvalue increased by adding terms to the model and the adjusted R-squared value decreased by adding non-significant terms to the model. Therefore, if multiple R-squared and adjusted R-squared values are different, it will indicate a good chance for non-significant terms to be included in the model [39-42]. The lack-of-fit value of the model determines data variation around the fitted model and must be insignificant in a well-fitted model.The lack-of-fit value of the model was 0.2, which indicates the presence of a significant correlation between independent variables and arsenite removal efficiency as response [35,38].

4. Response Surface Methodology and Contour Plotting

The contour plots based on the presented model coefficients were applied to show the effects of different parameters and their interactions on the efficiency of arsenite adsorption onto ONC and are shown in Fig. 5(a)-(c). As shown in Fig. 5(a), the percentage of arsenite removal was altered by varying the surfactant dosage, and the variation of the adsorbent dosage did not affect the removal efficiency. However, the increase in the surfactant dosage from 0. 5 to 2.3 g L^{-1} resulted in an increase in the arsenite removal percentage from 30% to 80%, respectively, keeping the adsorbent dosageat 2 g L^{-1} and the contact time at 33 min. This reveals that an organic medium created in the nanoclay is very suitable for the adsorption of arsenite, as its large molecular size and also the high capacity of the nanoclay for enlarging its interlayer space (when this organic molecule is transferred to this space) can result inan increased tendency of the surface to absorb arsenic ions [25]. The BET analysis showed that the specific surface area in m^2/g increased from 4.46 m^2/g for the nanoclay to 61.99 m^2/g for ONC, and this demonstrates the increased efficiency of arsenite adsorption by ONC [19,25,43]. The BJH analysis revealedan increase in mean pore diameter of ONC in comparison with nanoclay, as mean pore diameter increased from 6.1 nm to 7.5 nm when the nanoclay was treated with organic materials [43,44]. Fig. 5(b) indicates the interactive effects of time and adsorbent dosage in the removal effi-

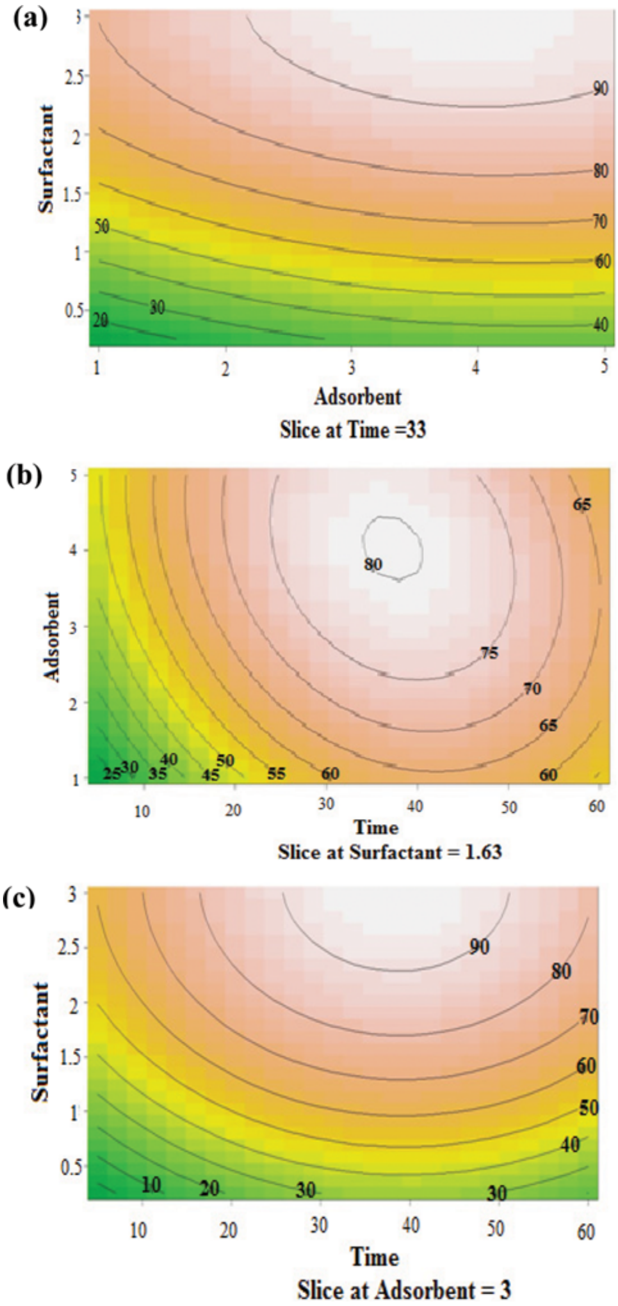

Fig. 5. Contour plots for the effect of (a) surfactant dose (g L^{-1}) and time, (b) adsorbent dose (g L^{-1}) and time, (c) surfactant dose (g L^{-1}) and adsorbent dose (g L^{-1}) on the arsenic removal.

ciency of ONC. Based on the results shown in Fig. 5(b), when the surfactant dose was kept constant at 1.63 g L^{-1}, at a certain time (e.g., 20 min), removal efficiency was increased with increasing adsorbent dosage from 1 to 4 g L^{-1}, and rose from 50% to 70%, respectively. Moreover, at a certain adsorbent dose, increasing the time up to 35 min increased removal efficiency, but increases above 35 min did not improve efficiency [25,43]. The maximum removal percentage of arsenite was observed at the adsorbent dosage of 3 g L^{-1} and contact time of 35 min. This can be attributed to more available sites and contact surfaces of the sorbent for adsorption, the diffusion of the arsenite into the bulk of the adsorbent (interior surface), and also the increase in the number of active and accessible linking sites for the sorbent [24,25]. The interactive effects of the surfactant dosage and time at a fixed dose of 3 g L^{-1} of the adsorbent are shown in Fig. 5(c): At a constant time (10 min), the removal percentage of arsenite rose from 10% to 60% with increasing surfactant dosage from 0.5 to 2.5 g L^{-1}. It reveals that surfactant dosage is a significant factor in promoting removal efficiency. The maximum arsenite removal (90%) was achieved for surfactant dosages higher than 2 g L^{-1} and contact times above 30 min. In all the contact times, minimum removal efficiency was obtained when surfactant dose was less than 0.5 g L^{-1}. In the entire surfactant dosages, increasing the time to 35 min improved removal efficiency, while increasing the time above 35 min did not significantly affect the removal percentage. It shows that increasing the time by keeping the amounts of surfactant and adsorbent at fixed values had no significant effect on the removal percentage, while increasing the surfactant dosage while keeping the amounts of surfactant and time at fixed values improved performance in the removal efficiency. It reveals that when organic molecules are transferred to the interlayer space of nanoclay, its large molecular size and also the adsorption capacity of the nanoclay are promoted, which can result in the increased tendency of the surface to absorb arsenic ions [2,24,29].

5. Process Optimization and Confirmation

The Solver software [39] was applied using effective parameters to obtain the optimum conditions for the model as predicted by RSM. These parameters included adsorbent dosage (1-3 g L^{-1}), surfactant dosage (0.94-3 g L^{-1}) and the time (5-60 min). The maximum removal efficiency in the predicted optimal conditions involving all parameters simultaneously was estimated as 95.95%. The predicted optimal conditions by the Solver "Add-ins" were an adsorbent dosageof 3.7 g L^{-1}, a surfactant dosageof 3 g L^{-1} and a time of 37.2 min. To confirm the validity of the predicted optimum conditions, laboratory experiments were done, and we found that the experimental data were in good consistency with the above-mentioned optimal conditions [37-42].

CONCLUSIONS

The quadratic model showed that adsorbent dosage (x_2), surfactant dosage (x_4) and time (x_5) have a significant role in response prediction by the model. Therefore, pH (x_1) and initial arsenic concentration (x_3) terms (p-values>0.05) were removed from the model and the model was developed in the presence of the adsorbent dosage, the surfactant dosage and time. These terms were entered into the model due to p-values<0.05. It was found that x_2, x_4 and x_5 have a synergistic effect on the response prediction by the model, while (x_4^2) and (x_5^2) were shown to have an antagonistic effect on the model. The reduced model was applied for prediction and optimization. Based on the analysis of variance for the model, ('P' lower than 0.01, R^2 (0.8) and the R^2 (adj) values (0.78) and lack of fit (0.2)), we can be certain of the satisfactory agreement of the quadratic regression model with the experimental data. The optimal operating point (adsorbent dose: 3.7 g L^{-1}, surfactant dose: 3 g L^{-1} and the time: 37.2 min) giving maximum arsenic removal was found by using Solver "Add-ins" in Microsoft Excel 2010.

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