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Simultaneous removal of As(III) and As(V) from wastewater by co-precipitation using an experimental design approach

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ABSTRACT

Response surface methodology (RSM) with central composite design was used to determine the significant effects of pH, ferric ion, and initial arsenic concentrations on the removal efficiency of arsenic by a co-precipitation method. The regression function, with coefficients calculated by multiple linear regression, was calibrated and validated using external experimental runs. The correlation coefficients (R^2) of the actual vs. predicted arsenic removal percentages were 0.9871 and 0.9478 for As(III) and As(V), respectively. All major factors were determined to be significant by analysis of variance, with p-values < 0.01 and had a district effort on the removal process. Multi-layer response surfaces were developed to determine the highest removal efficiency. The maximum removal efficiencies for arsenic species were approximately 100%, achieved by model prediction with a Fe/As mole fraction of 3.34 at pH 7. These optimized conditions were then applied to remove arsenic from two industrial wastewater samples, giving efficiencies of 93.98 and 91.48%. The results reveal that the chosen conditions from the RSM approach are applicable for arsenic removal from real water samples, without any pretreatment process.

Keywords: Simultaneous removal; Arsenic; Central composite design; Response surface methodology; Wastewater

1. Introduction

Arsenic is a toxic element that shows detrimental effects on the environment, and exposure in human beings is linked to ailments such as skin and lung cancer, and other diseases [1]. Many millions of people have suffered from the effects of toxic arsenic contaminants in natural ground water [2,3] in countries such as Thailand [2], Bangladesh [4–6], USA [4], China [7], Australia [8], and Colombia [9]. The World Health Organization and the United States Environmental Protection Agency have set a 10 μg/L maximum threshold level for arsenic in drinking water. Additional forms and higher levels of arsenic contaminants can be released into water sources through human activities such as mining, use of agricultural pesticides, and refinery operations in the petroleum industry [10].

Several methods have been studied for removal of arsenic from water samples, such as co-precipitation

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or coagulation [11–14], adsorption [15–18], membrane filtration [19], and ion exchange [20–22]. Co-precipitation allows for decreases in turbidity and color elimination from wastewater and also effective removal of high degrees of arsenic contaminants, with an added benefit of being applicable to large-scale industrial processes. Ferric chloride has been shown as an effective coagulant for arsenic removal from water through co-precipitation due to a high removal efficiency and a wide pH range [12,23]. Removal efficiencies of almost 99% have been reported for As(V) [11–13]. However, removal efficiencies of As(III) are lower than that of As(V) at neutral pH range [11]. Thus, a pre-oxidation process is necessary to oxidize As(III) to As(V) prior to co-precipitation [24–26].

Obtaining maximum removal efficiencies for arsenic has been a main propose of several studies, and these involves systematic evaluation/variation of conditions affecting removal such as increasing coagulant dose, adding coagulant aids, and pH solution adjustment [11]. However, if the selected factors are shown to be correlated, the conditions chosen from the experimental work might not be satisfactory, and therefore misleading [27]. Therefore, combining careful experimental design with response surface methodology (RSM) is an effective strategy for deriving optimized conditions for arsenic removal using minimal experimentation. Demin et al. [28,29] demonstrated the application of central composite design (CCD) combined with RSM analysis to investigate the significant factors that influenced the heavy metal removal (Cd^{2+}, Cr^{6+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}) from aqueous solution using bioremoval process. Baskan and Pala reported the use of Box–Behnken statistical experiment design (BBD) to evaluate optimal conditions for As(V) removal by ferric ions [12], and aluminum sulfate [13]. Jaafarzadeh et al. were able to utilize volcanic ash adsorbent modified with Fenton reagent (Fe^{2+}/H_2O_2) for determining the removal of As(III) and As(V) ions by means of factorial experiment design [30]. Khan et al. studied arsenic removal efficiency using various adsorbents with the aid of statistical analysis and factorial design [31]. Such experimental design approaches for arsenic removal focused only on As(V) as removal of As(III), especially by co-precipitation, require pre-oxidation as indicated earlier [25,26]. Oxidizing agents such as hypochlorite or potassium permanganate should be avoided to minimize treatment costs and prevent additions to the effluent waste stream. For these reasons, simultaneous removal of both arsenic species using an efficient coagulant (such as ferric ions) should be an attractive, industrially relevant, treatment process.

The objective of this work is to evaluate the removal efficiencies of As(III) and As(V) from water by ferric ions using CCD and study the main effects including ferric ion concentration, pH, and arsenic concentration, on the removal process. Besides, the system might have a serious problem when variables interact with each other. An experimental design approach whereby all factors are varied simultaneously is an important issue to be considered. The key advantages of our study are the discovery of an optimized condition for simultaneous removal of As(III) and As(V) with the high removal efficiencies without any pre-oxidation requirement. The regression function of the removal efficiency relating to the factors mentioned above was obtained using multiple linear regression (MLR), with calibration and validation steps demonstrated using external experimental runs to prevent problems of overfitting. Additionally, an alternative way to visualize the several response surfaces was developed using a superimposition approach for better viewing and interpretation. Using this, the optimized condition was determined as the condition having the highest removal efficiency as presented in the overlapped response surfaces for As(III) and As(V). The chosen condition was then applied to the removal of arsenic from setup mixtures, and real wastewater samples.

2. Experimental

2.1. Materials, reagents, and apparatus

Anhydrous iron(III) chloride was supplied by Merck. Stock solutions of 1,000 mg As(V)/L, and 1,000 mg As(III)/L were purchased from Sigma-Aldrich. Arsenic concentrations were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP 6500 DUO, Thermo Scientific).

2.2. Co-precipitation procedure

Ferric chloride was added, in separate experiments, to 10 mL of arsenic solution (each containing different concentrations of arsenic) followed by pH adjustment (HCl and/or NaOH). After that, the mixed solution was stirred rapidly for few minutes, followed by slow agitation for 30 min, and then followed by a precipitation time of 30 min. After co-precipitation, the solution was centrifuged at 3,200 rpm for 10 min, and the supernatant was stored for arsenic determination using ICP-OES.

2.3. Experimental design

The purpose of using experimental designs is to deliver as much information as possible with a minimum amount of experimentation and to develop a mathematical model to represent direct and interactive effects of the process factors [32]. In this study, the CCD was chosen for modeling and optimizing the simultaneous removal of As(III) and As(V) using a co-precipitant (ferric ions, Fe^{3+}). The setup experiments based on CCD were developed using three main factors: solution pH (X_1), concentration of ferric ions as co-precipitant (X_2), and initial arsenic concentration (X_3). All experiments were re-performed in triplicate to investigate the reproducibility of the data and to obtain a sound mathematical model. The domain ranges and the coded levels for the factors investigated in the study for both As(III) and As(V) are given in Table 1. In this case, the ranges of the three factors were chosen based on our preliminary experiments and previous research [12–15].

2.4. Response surface methodology (RSM)

By convention, the optimization of multifactor experiments is carried out by varying only a single factor at a time, while the other factors are fixed at specific conditions. The optimized conditions could be achieved in cases where there are no interactions between factors in experiments; however, individual factors rarely act independently in relation to the response. There are several disadvantages of this approach: it is time consuming, and best optimization cannot be realized as the interactive effects of all primary factors are neglected. RSM is an alternative technique whose main advantage is to represent the interactive effects of the primary factors correlated to the response [27]. It is very useful for developing, improving, and optimizing experimental conditions in order to obtain the most suitable response. In this study, the removal efficiency of As(III) and As(V) is strongly related to the setup factors (pH, concentration of co-precipitant, and initial arsenic concentration). It can be considered as a function of $y = f(X_1, X_2, \ldots, X_n)$ where y is the response removal efficiency of the system and $X_1, X_2, \ldots, X_n$ are considered in the function as the individual independent parameters. However, the interaction and the higher degree of the factors (e.g. quadratic etc.) can be also included in the function as model parameters. In our study, the parameters with individual, interaction, and second-order polynomial terms are constructed in the regression model in order to find an appropriate approximation of the function as in the following equation:

$$y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (1)$$

where b_0 is the intercept constant coefficient, and b_i, b_{ii}, b_{ij} are the coefficients for the linear, quadratic, and interaction effects, respectively.

To obtain the RSM of the process, it involves three main steps:

Step 1: careful design of the experiments: the statistically designed experiment using the CCD described in Section 2.3 is used in this step.

Step 2: evaluating the coefficients of the mathematical regression model: MLR technique [27,33] is used to calculate the coefficients of each term in the following regression model equation:

$$\boldsymbol{b} = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\boldsymbol{X}^{\mathrm{T}}\boldsymbol{y} \quad (2)$$

where T is the transpose operator, $\boldsymbol{X}$ is the experimental matrix, $\boldsymbol{y}$ is the response vector, and $\boldsymbol{b}$ represents the vector of the calculated coefficients for all parameters.

Step 3: calculate the predicted responses using the obtained regression model to produce the response surface to extrapolate the optimized condition.

Table 1
Experimental domain for As(III) and As(V)

Factor	Symbol		Range and coded level				
			−1.682	−1	0	1	1.682
pH	X_1	As(III)	5	6	7.5	9	10
		As(V)	4	5	6.5	8	9
[Fe^{3+}] (mg/L)	X_2	As(III) As(V)	23.85	75.00	150.0	225.0	276.0
[As] (mg/L)	X_3	As(III) As(V)	14.55	45.45	90.91	136.4	167.3

Moreover, the significance of each parameter and the adequacy of the model are assessed using the analysis of variance (ANOVA) approach [34]. Models and parameters with high F-values and probability values (Prob. $> F$) are considered significant. The correlation coefficient value (R^2) is used to evaluate the quality of the fit of the model [35]. Statistical and response surface analyses of the removal process were performed by employing a program developed in-house using MATLAB (Mathwork, Inc. Version R2011b).

2.5. Validation of the models

Nine independent experiments, each with three replications (total = 27 runs) were performed as an external validation set. The value of each factor in each experiment was randomly chosen within the ranges of the experimental domain shown in Table 1. The predicted response values of the 27 experiments were obtained using the regression function, and the correlation coefficient (R^2) was used to evaluate the quality and generality of the model. The optimized condition was chosen from the generated response surfaces, and the condition utilized in removal of arsenic species from prepared mixtures, and wastewater samples provided by a petroleum company in Thailand.

3. Results and discussion

3.1. Removal efficiency estimation

The procedure used for arsenic determination in the test solutions was based on the standard ICP-OES method [36]. The effect of co-precipitation time was evaluated over a range of 30 min to 5 h, using 10 mL of 100 mg As/L, and 1 mL of 1 g $FeCl_3$/L at pH 5. The removal efficiency defined as a removal percentage was calculated from Eq. (3), where C_i represents the initial concentration of arsenic in solution (mg/L), and C_r is the residual concentration of arsenic in the supernatant (mg/L).

$$\text{Removal percentage } = \frac{C_i - C_r}{C_i} \times 100 \tag{3}$$

The preliminary result (data not shown) revealed the removal efficiency of both As(III) and As(V) remained constant over time, and suggested that a precipitation time of 30 min was suitable for further studies.

3.2. Influence of the major factors in co-precipitation

The removal of arsenic by precipitation and co-precipitation using ferric ions (Fe^{3+}) has attracted much attention over many years. This approach has been recognized as the most effective and practical method for arsenic removal. Many studies have focused on the complexation between arsenic species and ferric ions [37,38], with the mechanism of the process being crucially important to the development of effective co-precipitation processes for arsenic removal.

The first step of the mechanism involves the dissolution of ferric chloride in the presence of arsenic species. As in the following equations, arsenic oxyanions can be precipitated in the form of ferric arsenite ($FeAsO_3$) and ferric arsenate ($FeAsO_4$), while ferric hydroxide can also be precipitated.

$$\mathrm{Fe^{3+}(aq) + \ AsO_3^{3-}(aq) \rightleftharpoons FeAsO_3(s)}$$

$$\mathrm{Fe^{3+}(aq) + \ AsO_4^{3-}(aq) \rightleftharpoons FeAsO_4(s)}$$

$$\mathrm{Fe^{3+}(aq) + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+(aq)}$$

In addition, ferric hydroxide has a high adsorptive capacity for As(V) and moderate adsorptive capacity for As(III) [11]. The arsenic species can associate with these co-precipitants occurring in solution via the formation of inner sphere surface complexes [37,39].

$$\mathrm{Fe(OH)_2(OH)(s) + H_3AsO_3(aq) \rightleftharpoons [Fe(OH)_2HAsO_3^-](s) + H^+(aq) + \ H_2O}$$

$$\mathrm{Fe(OH)_2(OH)(s) + H_3AsO_4(aq) \rightleftharpoons [Fe(OH)_2AsO_4^{2-}](s) + 2H^+(aq) + \ H_2O}$$

At certain pH values, the following co-precipitation processes can take place.

$$\mathrm{H_2AsO_3^-(aq) \ + \ Fe(OH)_3(s) \rightleftharpoons Fe\text{–}As\ complex(s) + OH^-(aq)}$$

$$\mathrm{H_2AsO_4^-(aq) \ + \ Fe(OH)_3(s) \rightleftharpoons Fe\text{–}As\ complex(s) + \ OH^-(aq)}$$

According to the proposed mechanism, the key parameters for the successful removal of arsenic using ferric ions are the solution pH, and the concentrations of ferric ions, and arsenic. The ratio of ferric ions: arsenic concentration is a crucial factor in the method.

From the mechanism, it can be noted that the concentration of ferric ions should be higher than the arsenic species in order to ensure complete co-precipitation. Furthermore, pH plays an important role in the co-precipitation process as the distribution and mobility of solute species, especially As(III) and As(V), are known to be pH dependent [37]. These parameters strongly correlate with the co-precipitation mechanism, thus influencing arsenic removal, and therefore it is critical to determine the optimized conditions for these major factors for the development of new water treatment processes.

3.3. Central composite designs

Among the standard experimental design models, the CCD represents a good option because of its high efficiency, and being rotatable and orthogonal, which allows for optimized process conditions to be derived from a minimum number of required experiments [34]. CCD construction is simple since they are based on multilevel factorials, additional axial points and center points. In our case, the experimental runs were repeated six times for the center point and three times for the other points in order to improve the precision of the experiments, and to ensure good reproducibility for the removal process and measurement stability. Therefore, the total number of experimental runs in our CCD was 48. The experiments were run in a random manner to minimize background errors generated by the effects of uncontrolled variables. The factors and their levels in each experimental run were constructed based on the experimental domain in Table 1. From the domain, the working pH ranges for As(III) and As(V) are slightly different, this being based on the fact that anionic species such as $H_2AsO_3^-$ and $H_2AsO_4^-$ could favor co-precipitation. The predominant aqueous As(III) species is $H_2AsO_3^-$ when the pH is higher than 9.2 (thus the working pH range was assigned to 5–10), while the predominant aqueous As (V) species are $H_2AsO_4^-$ and $HAsO_4^{2-}$ when the pH is between 4 and 10 [2]. The designed matrix and the average responses (removal efficiency) of each design point are shown in Table 2. Only small variations in the detected responses in each run were observed, suggesting that the measurements were reproducible with high precision.

A regression model including quadratic parameters correlating the arsenic removal efficiency with interactive parameters was calculated though MLR. The proposed constructed function has 10 parameters consisting of one constant effect (intercept), three primary effects, three curvature effects and three two-factor interaction effects. After performing MLR to obtain the parameter coefficients, the following quadratic regression model shown in Eqs. (4) and (5), calculated using coded values, can be used to express the removal efficiency of As(III) and As(V), respectively.

$$y_{\mathrm{As(III)}} = 81.65 + 1.53X_1 + 18.51X_2 - 10.40X_3 - 1.89X_1^2 - 8.09X_2^2 - 0.97X_3^2 + 0.02X_1X_2 + 0.20X_1X_3 + 2.97X_2X_3 \quad (4)$$

Table 2
The designed matrix and the responses for a CCD for As(III) and As(V) removal

	Coded level			% Removal[a]	
Experimental run	X_1	X_2	X_3	As(III)	As(V)
1	−1	−1	−1	63.33 ± 0.71	99.07 ± 0.10
2	1	−1	−1	70.30 ± 0.32	84.76 ± 0.42
3	−1	1	−1	92.92 ± 0.21	99.90 ± 0.00
4	1	1	−1	96.73 ± 0.11	98.60 ± 0.03
5	−1	−1	1	37.73 ± 0.48	49.17 ± 0.97
6	1	−1	1	42.25 ± 0.36	42.58 ± 1.98
7	−1	1	1	75.95 ± 0.30	99.14 ± 0.23
8	1	1	1	83.82 ± 0.17	87.76 ± 0.20
9	0	0	0	81.58 ± 0.42	94.60 ± 2.97
10	0	−1.682	0	24.41 ± 0.60	25.39 ± 0.66
11	0	1.682	0	93.99 ± 0.09	99.38 ± 0.03
12	0	0	1.682	61.94 ± 0.10	66.99 ± 0.49
13	0	0	−1.682	96.75 ± 0.76	99.72 ± 0.10
14	−1.682	0	0	77.43 ± 0.45	99.78 ± 0.05
15	1.682	0	0	76.09 ± 0.74	76.52 ± 1.45

[a] An average and variation of removal percentage for As(III) and As(V) ($n = 3$).

$$y_{\mathrm{As(V)}} = 94.06 - 5.32X_1 + 17.15X_2 - 11.62X_3 - 0.96X_1^2 - 10.07X_2^2 - 2.66X_3^2 + 1.03X_1X_2 - 0.29X_1X_3 + 10.06X_2X_3 \quad (5)$$

The sign of the coefficient (positive or negative) indicates the direction of the effect. A positive effect means that the response is enhanced when the parameter level increases, and a negative effect shows that the response is reduced when the factor level increases. The size of the effect is denoted by the magnitude. Basically, parameters that are demonstrably larger in magnitude will have greater significance compared with small magnitude parameters. Interestingly, the opposite coefficient signs of X_1 factor (solution pH) which is positive for As(III) and negative for As(V) were noticed. This suggests that monovalent anions ($H_2AsO_3^-$ and $H_2AsO_4^-$) are preferred in the co-precipitation process. For As(III), when the pH is increased from 7 to 10, the relative fraction of $H_2AsO_3^-$ increases, meanwhile in case of As(V), when the pH is lowered from 9 to 4, the fraction of $H_2AsO_4^-$ increases [2]. This observation was in a good agreement with experimental results reported by Meng et al. [39]. Thus in this case, a "One-factor at a time" method is not satisfactory for simultaneous removal of As(III) and As(V), therefore it is necessary to apply the RSM approach.

Table 3
ANOVA of the quadratic regression model for As(III) and As(V) to determine the significance of the effects in the system

Parameters	Sum of squares	DF[a]	Mean square	*F*-value	*p*-value
As(III) removal					
Model	20,831.91	9	2,314.66	321.98	<0.0001[b]
X_1	96.22	1	96.22	13.38	0.0008[b]
X_2	14,042.32	1	14,042.32	1,953.33	<0.0001[b]
X_3	4,435.23	1	4,435.23	616.95	<0.0001[b]
X_1^2	132.07	1	132.07	18.37	0.0001[b]
X_2^2	2,427.03	1	2,427.03	337.61	<0.0001[b]
X_3^2	35.16	1	35.16	4.89	0.0331[c]
X_1X_2	0.01	1	0.01	0.00	0.9643[c]
X_1X_3	0.99	1	0.99	0.14	0.7125[c]
X_2X_3	211.92	1	211.92	29.48	<0.0001[b]
Residual	273.18	38	7.19		
Lack of fit	266.87	5	53.37	279.02	<0.0001[b]
pure error	6.31	33	0.19		
Total	21,105.09	47			
R^2	0.9373				
As(V) removal					
Model	24,400.34	9	2,711.15	76.73	<0.0001[b]
X_1	1,160.53	1	1,160.53	32.85	<0.0001[b]
X_2	12,054.13	1	12,054.13	341.17	<0.0001[b]
X_3	5,533.66	1	5,533.66	156.62	<0.0001[b]
X_1^2	34.26	1	34.26	0.97	0.3310[c]
X_2^2	3,755.95	1	3,755.95	106.30	<0.0001[b]
X_3^2	261.72	1	261.72	7.41	0.0097[b]
X_1X_2	25.35	1	25.35	0.72	0.4023[c]
X_1X_3	2.06	1	2.06	0.06	0.8103[c]
X_2X_3	2,428.99	1	2,428.99	68.75	<0.0001[b]
Residual	1,342.61	38	35.33		
Lack of fit	1,305.11	5	261.02	229.69	<0.0001[b]
Pure error	37.50	33	1.14		
Total	25,742.95	47			
R^2	0.9478				

[a] Degree of freedom.

[b] Significant at $p < 0.01$.

[c] Not significant at $p > 0.01$.

To evaluate the significance of the effects (parameters) on the process, ANOVA was performed. The results of ANOVA calculations through *F*-statistics and *p*-values for the quadratic models of As(III) and As(V) are shown in Table 3. High *F*-values and low pure errors are considered as required fit criteria for an applicable model. In the study, the model with *F*-values of 321.88 and 76.73 for As(III) and As(V), respectively, implies significance with only <0.01% chance that the large model *F*-value could occur due to noise. The model parameters are predicted to be significant for *p*-value less than 0.01, while greater than 0.01 are not significant. The significant model parameters for both arsenic species are indicated in Table 3, highlighted by a superscripted "s" symbol. From the ANOVA test, it is evident that the linear parameters of pH (X_1), concentration of ferric ion (X_2), and initial concentration of arsenic species (X_3) are significant with small *p*-values (<0.0001) for both As(III) and As(V) removal. This denotes that the chosen factors have high proportionality in relation to the removal efficiency, and the domain of the chosen factors is reasonable to be used for an approximation of the regression model. In fact, the factor pH plays an important role in the system as mentioned earlier. Only the quadratic parameter for ferric ion concentration is significant for the removal of arsenic species. The sign and significant effect of the parameter X_2 ($b_2 > 0$ and $b_{22} < 0$) indicates that there is an optimized point of X_2 in the experimental domain giving the highest removal efficiency. As seen by the co-precipitation mechanism, the higher the molar ratio of ferric ions to other components, the greater the removal efficiency. Additionally, it should be noted that only interaction effect (X_2X_3) was shown to significantly affect the response, as indicated by the *p*-value (<0.0001). The interaction refers that the concentration of ferric ions (X_2) has a different effect on the removal efficiency, depending on the concentration of arsenic species (X_3). By considering the sign of X_2, X_3 and this interaction terms, it indicates that the good response can be obtained by increasing effect of X_2 and decreasing effect of X_3. This observation is substantiated by the fact that a higher molar ratio of Fe/As facilitates the favorable co-precipitation process [11].

Examination of the correlation coefficients (R^2) has a quality of fit of 0.9871 and 0.9478 for As(III) and As(V), respectively. A correlation plot of the predicted vs. actual arsenic removal percentage is shown in Fig. 1(A). The actual values are the measured response data for particular runs, and the predicted values were evaluated using the regression function generated in Eqs. (4) and (5) to calibrate the model. In this study, we refer to this step as the model calibration. The results indicate that the model provides a sufficient representation of the real relationship among these variables. The accumulation of the points around the fitted line indicates a satisfactory correlation between the experimental data and the predicted values, demonstrating that the regression model is appropriate for predicting the response.

The regression model was generated and calibrated using the experimental points in the domain, as listed in Table 1. However, there is no guarantee that the model can be used to predict correctly the response of experiments undertaken using different conditions. A validation protocol is therefore necessary to describe the generality of the model, and to prevent errors from overfitting [40]. This protocol is required prior to producing the response surface in order to determine the real-optimized conditions, as it shows the ability to reproduce the system in either different laboratories or under different experimental circumstances. In this

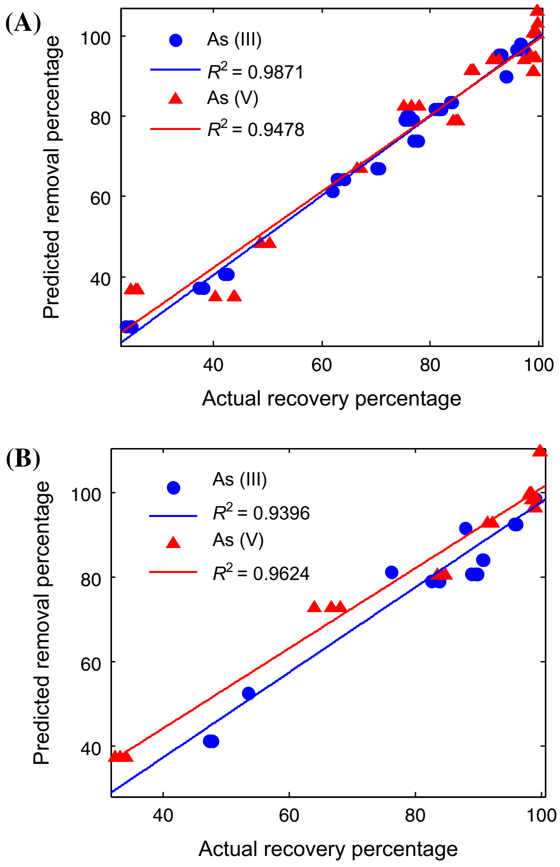

Fig. 1. Correlation of the actual (observed) and the predicted removal percentages for As(III) and As(V) represented in blue circle (●) and red triangle (▲), respectively, using the calculated regression model for (A) calibration and (B) validation.

case, the regression model was validated using nine extra experiments, with 3 replicates in each experiment generating 27 total runs. The experimental conditions were randomly chosen within the range of the experimental domain (Table 1) but not using the same points in the calibration set. Table 4 highlights the experimental conditions and the corresponding responses of the validation set for As(III) and As(V), with the correlation plot of the predicted and observed arsenic removal percentages being shown in Fig. 1(B). From this, the correlation coefficients (R^2) are 0.9326 and 0.9624 for the removal of As(III) and As(V), respectively, indicating that the R^2 is improved for As(V) and slightly decreased for As(III). However, the good correlation between predicted and observed response, especially for the external validation set, suggests that the obtained regression function (Eqs. (4) and (5)) does not suffer from overfitting and can be applied to the derivation of optimized conditions for the recovery of As(III) and As(V).

3.4. Response surface methodology (RSM)

The main objective of the RSM method is to facilitate the optimum condition from the response surface influenced by various factors, and to quantify the relationship between the controllable input parameters and the corresponding response surfaces. To have a better illustration of the results and to understand the relationships between the major factors, three-dimensional response surface plots of the As(III) and As(V) removal percentages are presented in Fig. 2(A) and (B), respectively. Generally, the axes in the surface plot can be selected as interaction statements having the largest absolute coefficients in the model, and p-values < 0.01. In our case, only the interaction of

Table 4
The designed matrix and the responses of the nine extra experimental set for As(III) and As(V) removal to use for the model validation. (X_1 = pH, X_2 = ferric ion concentration, and X_3 = initial concentration of arsenic)

As(III)					As(V)				
	Actual value (coded value)					Actual value (coded value)			
Run	X_1	X_2	X_3	Response	Run	X_1	X_2	X_3	Response
1	9.4 (1.3)	150 (0)	90 (0)	89.83	1	7 (0.34)	225 (1)	90 (0)	98.30
2	9.4 (1.3)	150 (0)	90 (0)	88.87	2	7 (0.34)	225 (1)	90 (0)	98.51
3	9.4 (1.3)	150 (0)	90 (0)	89.57	3	7 (0.34)	225 (1)	90 (0)	98.12
4	7 (−0.3)	225 (1)	90 (0)	96.05	4	5 (−1)	150 (0)	90 (0)	98.93
5	7 (−0.3)	225 (1)	90 (0)	95.82	5	5 (−1)	150 (0)	90 (0)	99.07
6	7 (−0.3)	225 (1)	90 (0)	95.98	6	5 (−1)	150 (0)	90 (0)	99.16
7	7.7 (0.1)	225 (1)	45 (−1)	98.93	7	5 (−1)	75 (−1)	90 (0)	64.04
8	7.7 (0.1)	225 (1)	45 (−1)	99.02	8	5 (−1)	75 (−1)	90 (0)	66.74
9	7.7 (0.1)	225 (1)	45 (−1)	99.09	9	5 (−1)	75 (−1)	90 (0)	68.17
10	5.2 (−1.5)	150 (0)	90 (0)	82.63	10	7.7 (0.81)	75 (−1)	45 (−1)	84.10
11	5.2 (−1.5)	150 (0)	90 (0)	83.76	11	7.7 (0.81)	75 (−1)	45 (−1)	83.51
12	5.2 (−1.5)	150 (0)	90 (0)	83.79	12	7.7 (0.81)	75 (−1)	45 (−1)	84.85
13	7.7 (0.1)	225 (1)	135 (1)	90.89	13	7.7 (0.81)	225 (1)	45 (−1)	98.86
14	7.7 (0.1)	225 (1)	135 (1)	90.79	14	7.7 (0.81)	225 (1)	45 (−1)	98.81
15	7.7 (0.1)	225 (1)	135 (1)	90.69	15	7.7 (0.81)	225 (1)	45 (−1)	99.02
16	7.7 (0.1)	75 (−1)	135 (1)	47.91	16	5.2 (−0.87)	150 (0)	90 (0)	98.39
17	7.7 (0.1)	75 (−1)	135 (1)	47.43	17	5.2 (−0.87)	150 (0)	90 (0)	98.82
18	7.7 (0.1)	75 (−1)	135 (1)	47.50	18	5.2 (−0.87)	150 (0)	90 (0)	98.73
19	9 (1)	75 (−1)	90 (0)	53.55	19	5.2 (−0.87)	150 (0)	14 (−1.7)	99.76
20	9 (1)	75 (−1)	90 (0)	53.55	20	5.2 (−0.87)	150 (0)	14 (−1.7)	99.89
21	9 (1)	75 (−1)	90 (0)	53.55	21	5.2 (−0.87)	150 (0)	14 (−1.7)	99.91
22	6 (−1)	150 (0)	90 (0)	76.20	22	7.7 (0.81)	225 (1)	135 (1)	91.52
23	6 (−1)	150 (0)	90 (0)	76.20	23	7.7 (0.81)	225 (1)	135 (1)	91.49
24	6 (−1)	150 (0)	90 (0)	76.20	24	7.7 (0.81)	225 (1)	135 (1)	92.32
25	6 (−1)	225 (1)	90 (0)	87.90	25	7.7 (0.81)	75 (−1)	135 (1)	33.26
26	6 (−1)	225 (1)	90 (0)	87.90	26	7.7 (0.81)	75 (−1)	135 (1)	34.27
27	6 (−1)	225 (1)	90 (0)	87.90	27	7.7 (0.81)	75 (−1)	135 (1)	32.42

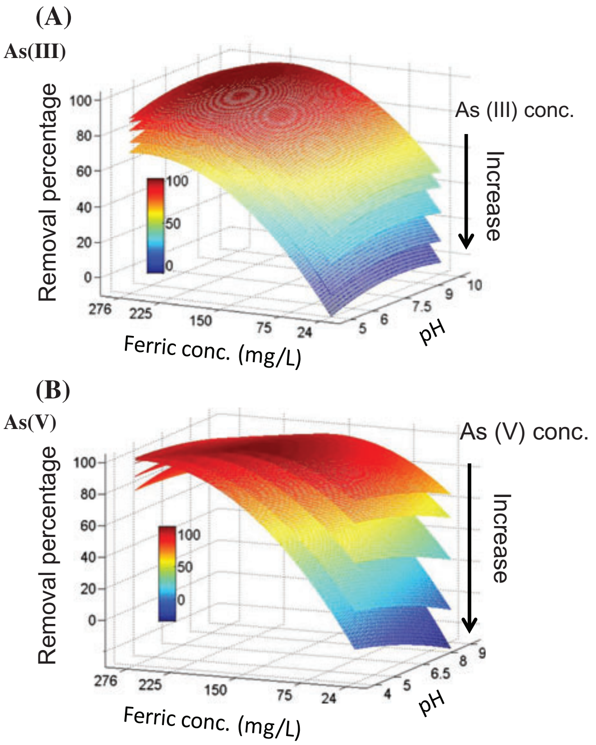

Fig. 2. Estimated response surface of the arsenic removal percentage by plotting pH vs. ferric ion concentration with superimposition of surface layers which represent different initial arsenic concentrations for (A) As(III) and (B) As(V).

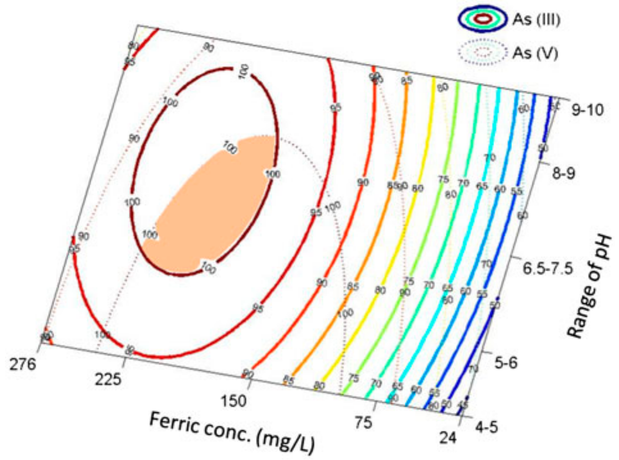

Fig. 3. Superimposition of response surfaces of the arsenic removal percentages by plotting pH vs. ferric ion concentrations at the lowest initial arsenic concentration for As (III): solid line, and As(V): dotted line. X-axis is labeled as the range of pH with lower bound: pH for As(V), and higher bound: pH for As(III). The range of the optimal conditions for arsenic removal is chosen from the overlapped area labeled in orange.

$X_2 \cdot X_3$ is significant from the ANOVA test. Plotting the surface response using the interaction of factors X_2 and X_3 might not provide an adequate interpretation as the individual factor X_1 (pH) is also significant and, interestingly, opposite signs for the parameter coefficient are observed for As(III) and As(V). Moreover, the initial arsenic concentrations may vary in different applications. Therefore, we attempt to present all interactions in one surface plot by setting the x- and y-axis to be X_1 (pH) and X_2 (ferric ion concentration), respectively, together with the surface layers corresponding to the different initial arsenic concentrations being superimposed in order to include all interactions of factors X_1, X_2, and X_3. Fig. 2 shows that the removal efficiency increases on increasing the co-precipitant concentration, while it remains unchanged at different pH values. However, the recovery efficiency varies dramatically with initial arsenic concentration, especially for the removal process of As(V). From the superimposed surface plots, it can be noted that the removal efficiency decreases as the initial arsenic concentration is increased. This is in good agreement with the regression functions (Eqs. (4) and (5)) where a negative sign for factor X_3 was observed in both removal processes. Consequently, the highest removal percentage will be found when the initial arsenic concentration is lowest.

To better visualize how the optimized conditions were obtained, the superimposed contour plots of the removal percentages using the lowest initial arsenic concentration are shown in Fig. 3. The surface contour

Table 5
The prepared mixtures of As(III) and As(V) and wastewater provided from petrochemical industry, the amount of total arsenic in wastewater is determined by ICP-OES

	Mixtures of As(III) and As(V)						Wastewater	
As species	1	2	3	4	5	6	TK80	TK81
As(III) (mg/L)	90.00	72.00	54.00	36.00	18.00	0.00	–	–
As(V) (mg/L)	0.00	18.00	36.00	54.00	72.00	90.00	–	–
Total As (mg/L)	90.00	90.00	90.00	90.00	90.00	90.00	66.31	68.16

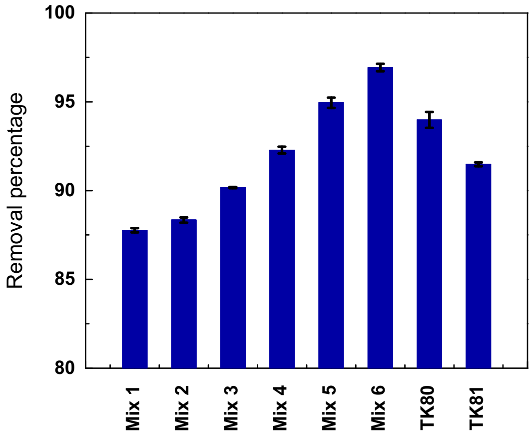

Fig. 4. Results of arsenic recovery percentages for the mixtures (Mix 1–6), and the wastewater provided from petrochemical industry (TK80 and TK81) determined using the optimal conditions obtained from the RMS method (pH 7 and 225 mg/L of ferric ions).

plots were obtained by varying simultaneously the two factors which are pH and ferric ion concentration. Only the range of preset pH (pH 4–10) and Fe dosage (24–276 mg/L) was considered and was used to calculate the removal efficiency. Solid and dotted lines in the contour plot represent the responses of As(III) and As(V), respectively, and the *x*-axis is labeled as the solution pH range in accordance with the different pH domains in the CCD (lower bound: pH for As(V) and upper bound: pH for As(III)). A perfect removal efficiency (100%) was found at the high ferric ion concentration, and over a pH range of 6–8 for both arsenic species. The area of 100% removal efficiency for As(V) is broader than that for As(III) because As (V) can more easily attach to the surface of ferric hydroxides, as reflected by the equilibrium constants (log *K*) of surface complexes of −3.1 for As(III), and 0.6 for As(V) [39]. Optimized conditions for simultaneous removal of As(III) and As(V) were chosen from the overlapped contour area (labeled in orange). From this, pH 7 and a ferric ion concentration of 225 mg/L (corresponding to 0.4 mg As removed/mg Fe^{3+} used) were identified as the optimum conditions for simultaneous As(III) and As(V) removal.

3.5. Application in mixtures and wastewater samples

The maximum removal efficiency of As(III) and As (V) was predicted from the RSM method using the following conditions: pH 7 and a ferric ion concentration

Table 6
Comparison of removal efficiencies of As(III) and As(V) using an experimental design approach

As species	Method	Experimental design	Major factors	Removal efficiency
As(V) [12]	Coagulation Flocculation	Box–Behnken	pH Coagulant dose (Fe^{2+}, Fe^{3+}) As concentration (10 μg/L^{-1} mg/L)	91–100%
As(V) [13]	Coagulation	Box–Behnken	pH Coagulant dose (Al^{3+}) As concentration (10 μg/L^{-1} mg/L)	91–100%
As(III), As(V) [30]	Oxidation–adsorption	Factorial design	pH Time Fe^{2+}/H_2O_2 dose	39 μg As^{III}/mg 41 μg As^{V}/mg
Not specified oxidation state [31]	Adsorption	Factorial design	Time Temperature pH As concentration (0.01–0.1 mg/L)	85–98%
As(III), As(V) [41]	Adsorption	Box–Behnken	pH As concentration (0.5–1 mg/L) Temperature	41 μg As^{III}/g 49 μg As^{V}/g
As(III) [42]	Electro-coagulation	CCD	Current density pH Aeration intensity Operating time	>99.94% [As] = 0.5 mg/L
As(III), As(V) [This work]	Co-precipitation	CCD	pH Coagulant dose (Fe^{3+}) As concentration (14–90 mg/L)	92–100%

of 225 mg/L. Six mixtures of As(III) and As(V) at different ratios, and wastewater samples from the petroleum industry were used in order to demonstrate the efficiency and effectiveness of the removal process. For the study, the total arsenic concentration in each mixture was maintained at 90 mg/L and the arsenic concentration in the wastewater samples (66–68 mg/L) was determined using ICP-OES. The sample details are shown in Table 5. Recovery percentages of the experiments, including the variations performed at the optimized condition settings, are illustrated in Fig. 4. For the mixture samples, the recovery percentage of arsenic species is in range of 88–98% with small standard variation (error scaled bar) as calculated from three repeated runs. This indicates that the chosen conditions are promising, from the high removal efficiency and good reproducibility. Interestingly, a decrease in removal efficiency in mixtures with higher ratio of As(III) occurred, due to the low equilibrium constant for surface complex formation [39]. In case of the wastewater samples, more than 90% removal was observed using the optimized conditions. The real samples contained As(III), As(V), and organic arsenic (unpublished data) which could possibly affect the removal efficiency. In addition, the samples might contain phosphate ions which affected the removal efficiency [11].

The comparison of our finding with the literature for the arsenic removal is presented in Table 6. This indicated the usefulness of the RSM method in the derivation of such conditions, and outlining the potential of co-precipitation as a low cost, environmentally cleaner industrial wastewater treatment process for arsenic removal.

4. Conclusion

A co-precipitation method using ferric ions for the effective and simultaneous removal of As(III) and As (V) species from wastewater was developed. CCD was set up to investigate the effects of solution pH, ferric ion, and initial arsenic concentrations on the removal efficiency. The regression model was calculated and validated using external experimental runs to address the concerns regarding the potential for overfitting. The correlation coefficients (R^2) value of the regression model shows a good fit of the models with experimental data for As(III) and As(V). The parameters selected by ANOVA show significant effects on the removal efficiency. In addition, pH and ferric ion concentration established to strongly influence the removal process. The response surface method was performed to investigate the effects of all interaction and to facilitate the optimized condition on the removal efficiency. The optimal conditions (pH 7 and 0.4 mg As removed/mg Fe^{3+} used) for simultaneous removal of As(III) and As (V) were derived from the overlapping contour regions having perfect removal efficiencies. Application of these conditions for arsenic removal from real samples resulted in more than 90% removal efficiency, without the necessity for addition of further oxidizing agent. Such co-precipitation processes therefore have real potential for integration into large-scale water management practices, with the added benefit of being lower cost and more environmentally benign.

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References

[1] S. Winski, D. Carter, Arsenate toxicity in human erythrocytes: Characterization of morphologic changes and determination of the mechanism of damage, J. Toxicol. Environ. Health A 53 (1998) 345–355.

[2] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.

[3] A. Basu, D. Saha, R. Saha, T. Ghosh, B. Saha, A review on sources, toxicity and remediation technologies for removing arsenic from drinking water, Res. Chem. Intermed. 40 (2014) 447–485.

[4] S.R. Wickramasinghe, B. Han, J. Zimbron, Z. Shen, M.N. Karim, Arsenic removal by coagulation and filtration: Comparison of groundwaters from the United States and Bangladesh, Desalination 169 (2004) 231–244.

[5] R. Nickson, J. McArthur, W. Burgess, K. Matin Ahmed, P. Ravenscroft, M. Rahman, Arsenic poisoning of Bangladesh groundwater, Nature 395 (1998) 338.

[6] X. Meng, G.P. Korfiatis, C. Christodoulatos, S. Bang, Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system, Water Res. 35 (2001) 2805–2810.

[7] Y. Deng, Y. Wang, T. Ma, Y. Gan, Speciation and enrichment of arsenic in strongly reducing shallow aquifers at western Hetao Plain, northern China, Environ. Geol. 56 (2009) 1467–1477.

[8] S.J. Appleyard, J. Angeloni, R. Watkins, Arsenic-rich groundwater in an urban area experiencing drought and increasing population density, Perth, Australia, Appl. Geochem. 21 (2006) 83–97.

[9] D.L. Alonso, S. Latorre, E. Castillo, P.F.B. Brandão, Environmental occurrence of arsenic in Colombia: A review, Environ. Pollut. 186 (2014) 272–281.

[10] B.K. Mandal, K.T. Suzuki, Arsenic round the world: A review, Talanta 58 (2002) 201–235.

[11] J. Qiao, Z. Jiang, B. Sun, Y. Sun, Q. Wang, X. Guan, Arsenate and arsenite removal by $FeCl_3$: Effects of pH, As/Fe ratio, initial As concentration and co-existing solutes, Sep. Purif. Technol. 92 (2012) 106–114.

[12] M. Bilici Baskan, A. Pala, Determination of arsenic removal efficiency by ferric ion using response surface methodology, J. Hazard. Mater. 166 (2009) 796–801.

[13] M. Bilici Baskan, A. Pala, A statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate, Desalination 254 (2010) 42–48.

[14] J.G. Hering, P.Y. Chen, J.A. Wilkie, M. Elimelech, Arsenic removal from drinking water during coagulation, J. Environ. Eng. 123 (1997) 800–807.

[15] M. Gallegos-Garcia, K. Ramírez-Muñiz, S. Song, Arsenic removal from water by adsorption using iron oxide minerals as adsorbents: A Review, Miner. Process. Extr. Metall. Rev. 33 (2012) 301–315.

[16] V.K. Gupta, V.K. Saini, N. Jain, Adsorption of As(III) from aqueous solutions by iron oxide-coated sand, J. Colloid Interface Sci. 288 (2005) 55–60.

[17] A.V. Vitela-Rodriguez, J.R. Rangel-Mendez, Arsenic removal by modified activated carbons with iron hydro(oxide) nanoparticles, J. Environ. Manage. 114 (2013) 225–231.

[18] J.C. Hsu, C.J. Lin, C.H. Liao, S.T. Chen, Removal of As(V) and As(III) by reclaimed iron-oxide coated sands, J. Hazard. Mater. 153 (2008) 817–826.

[19] B. Han, T. Runnells, J. Zimbron, R. Wickramasinghe, Arsenic removal from drinking water by flocculation and microfiltration, Desalination 145 (2002) 293–298.

[20] A. Oehmen, R. Valerio, J. Llanos, J. Fradinho, S. Serra, M.A.M. Reis, J.G. Crespo, S. Velizarov, Arsenic removal from drinking water through a hybrid ion exchange membrane—Coagulation process, Sep. Purif. Technol. 83 (2011) 137–143.

[21] B. Pakzadeh, J.R. Batista, Surface complexation modeling of the removal of arsenic from ion-exchange waste brines with ferric chloride, J. Hazard. Mater. 188 (2011) 399–407.

[22] B. An, Q. Liang, D. Zhao, Removal of arsenic(V) from spent ion exchange brine using a new class of starch-bridged magnetite nanoparticles, Water Res. 45 (2011) 1961–1972.

[23] C.K. Jain, R.D. Singh, Technological options for the removal of arsenic with special reference to South East Asia, J. Environ. Manage. 107 (2012) 1–18.

[24] X. Guan, J. Ma, H. Dong, L. Jiang, Removal of arsenic from water: Effect of calcium ions on As(III) removal in the $KMnO_4$–Fe(II) process, Water Res. 43 (2009) 5119–5128.

[25] T. Nishimura, Y. Umetsu, Oxidative precipitation of arsenic(III) with manganese(II) and iron(II) in dilute acidic solution by ozone, Hydrometallurgy 62 (2001) 83–92.

[26] S. Sorlini, F. Gialdini, Conventional oxidation treatments for the removal of arsenic with chlorine dioxide, hypochlorite, potassium permanganate and monochloramine, Water Res. 44 (2010) 5653–5659.

[27] R.G. Brereton, Chemometrics, Wiley, Chichester, UK, 2003.

[28] S. Demim, N. Drouiche, A. Aouabed, T. Benayad, O. Dendene-Badache, S. Semsari, Cadmium and nickel: Assessment of the physiological effects and heavy metal removal using a response surface approach by *L. gibba*, Ecol. Eng. 61 (2013) 426–435.

[29] S. Demim, N. Drouiche, A. Aouabed, T. Benayad, M. Couderchet, S. Semsari, Study of heavy metal removal from heavy metal mixture using the CCD method, J. Ind. Eng. Chem. 20 (2014) 512–520.

[30] N. Jaafarzadeh, H. Amiri, M. Ahmadi, Factorial experimental design application in modification of volcanic ash as a natural adsorbent with Fenton process for arsenic removal, Environ. Technol. 33 (2012) 159–165.

[31] M.H. Khan, M. Tariq, F. Bashir, T. Shafiq, R.A. Khan, J. Jung, Arsenic removal from drinking water with conventional and modified adsorbents: The factorial design of experiments, Desalin. Water Treat. 51 (2013) 7304–7310.

[32] P.J. Gemperline, practical Guide to Chemometrics, seventh ed., Taylor & Francis Group, Boca Raton, 2006.

[33] R.G. Brereton, Applied Chemometrics for Scientists, Wiley, Chichester, UK, 2007.

[34] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, fourth ed., Prentice Hall, Harlow, England, 2000.

[35] S. Bajpai, S.K. Gupta, A. Dey, M.K. Jha, V. Bajpai, S. Joshi, A. Gupta, Application of central composite design approach for removal of chromium(VI) from aqueous solution using weakly anionic resin: Modeling, optimization, and study of interactive variables, J. Hazard. Mater. 227–228 (2012) 436–444.

[36] International Standards Organization, Water quality—Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES), ISO 11885, 2007.

[37] B.A. Manning, S.E. Fendorf, S. Goldberg, Surface structures and stability of arsenic(III) on goethite: Spectroscopic evidence for inner-sphere complexes, Environ. Sci. Technol. 32 (1998) 2383–2388.

[38] W. Driehaus, M. Jekel, U. Hildebrand, Granular ferric hydroxide—A new adsorbent for the removal of arsenic from natural water, J. Water Supply Res. T 47 (1998) 30–35.

[39] X. Meng, S. Bang, G.P. Korfiatis, Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride, Water Res. 34 (2000) 1255–1261.

[40] R.G. Brereton, Chemometrics for Pattern Recognition, Wiley, Chichester, UK, 2009.

[41] S.H. Hasan, D. Ranjan, M. Talat, “Rice Polish” for the removal of arsenic from aqueous solution: Optimization of process variables, Ind. Gen. Chem. Res. 48 (2009) 4194–4201.

[42] P. Song, Z. Yang, H. Xu, J. Huang, X. Yang, F. Yue, L. Wang, Arsenic removal from contaminated drinking water by electrocoagulation using hybrid Fe–Al electrodes: Response surface methodology and mechanism study, Desalin. Water Treat., doi: 10.1080/19443994.2014.992973.