Statistical analysis and process optimization for maximizing removal of As (III) and As (V) by coagulation/filtration method

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Abstract

The present study investigates arsenic removal using ferric ions by coagulation/filtration method in water/groundwater using design of experiment (DoE) approach and without incorporation of any pre-treatment steps. The effect of three process variables namely pH of liquid medium, contact time, and initial ferric ions Fe (III) concentration was studied and optimized using response surface methodology for maximizing the removal of arsenite [As (III)] and arsenate [As (V)].The studied synthetic water sample had an initial $100 \mu gL^{-1}$ concentration of As (III) and As (V) each and was removed using coagulation/filtration method. A quadratic model was obtained and validated using experimental runs.The results of analysis of variance (ANOVA) indicated that predicted results were in good agreement with the experimental output with the correlation coefficient (R^2) of 0.9383 and 0.9606 for the removal of As (III) and As (V) respectively. The pH and Fe (III) concentrations exhibit the most significant effect on As (III) and As (V) removal efficiency. The regression analysis showed linear relation and interaction effects were significant with the p-value < 0.01. The optimized values of test variables for As (III) and As (V) removal were found to be pH = 9 and 9.3,contact time was determined to be 10 min for As (III) and 15 min for As (V),Fe (III)=30 and 32 mgL^{-1}. These optimized conditions were applied to two groundwater samples from West Bengal (WB)[groundwater was present with only has As(V)].In groundwater sample, more than 80-85% removal of As (V) was observed with simultaneous removal of other heavy metals.

Keywords: Arsenic removal, response surface methodology, coagulation, filtration, groundwater

Abbreviations

As   Arsenic

Fe   Iron

DoE   Design of experiment

ANOVA   Analysis of variance

MCL   Maximum Contaminant Level

WHO   World Health Organization

NHMRC   National Health and Medical Research Organization

ICP-MS   Inductively coupled plasma-mass spectrometry

HPLC   High-performance liquid chromatography

TDS   Total dissolved solids

RSM   Response surface methodology

R.E   Removal efficiency

R %   Removal percentage

R^2 Correlation coefficient

WB   West Bengal

rpm   Revolution per minute

Eq   Equation

min   Minutes

mg   Milligram

µg   Microgram

L^{-1} Per liter

1. Introduction

Arsenic is one of the world's most hazardous chemical found to exist in surface water, shallow zones of groundwater and finished drinking water.The most common inorganic forms of arsenic are trivalent arsenite [As (III)] and pentavalent arsenate [As (V)] found in aerobic surface water and anaerobic groundwater respectively[1].Surface water and groundwater get contaminated by arsenic through dissolution, weathering of arsenic-containing minerals and certain anthropogenic sources to various degrees [2-5].One of the worst natural disasters on earth is arsenic poisoning in drinking water[6].World Health Organization[7] and National health and medical research committee (NHMRC) recommended the maximum contaminant level (MCL) of $10µgL^{-1}$ for arsenic in drinking water [4].

Arsenic enters the human body through drinking water as one of the most important media. Arsenic is well known for its carcinogenicity in skin, kidney, liver, lung, bladder, acute, and chronic metabolic disorders, such as dermal pigments (Blackfoot disease), arsenicosis, and hepatocellular carcinoma. That will result in slow and

painful death which may cause due to exposure to arsenic above $10\mu gL^{-1}$ via drinking water [8-12].Countries like Bangladesh, Thailand, Australia, Colombia, China, India, Chile, USA, Hungary, and Taiwan, has reported great adverse health effect due to exposure to arsenic contaminated water. Among which the most severely affected countries in Asia are Bangladesh, India (West Bengal), Inner Mongolia, China and Taiwan[2-3]. In these countries, groundwater uptake was increased due to the agricultural irrigation[23]. Over 50% of the global population used groundwater for the potable purpose and sometimes described as the 'hidden sea'[10]. Natural water sources contain a much higher level of arsenic $(20\text{-}3000\mu gL^{-1})$[1]. In Bangladesh, nearly 59 districts amounting to about 80 million people are exposed to arsenic-contaminated water[13]. West Bengal in India and Bangladesh are reported to be the most arsenic affected areas in the world [14].

As (V) is relatively easy to remove from water than As (III) since it bears a negative charge above the pH 2.2 in natural water. Therefore, it is electro-statistically attracted to the positive charge on metal hydroxide surface[1].There are several physical and chemical treatment methods for removing arsenic in water matrix like ion-exchange, electro-coagulation, coagulation, filtration, air-oxidation, chemical-oxidation/reduction, precipitation, co-precipitation, adsorption, membrane technologies, solvent-extraction and bioremediation. Coagulation and precipitation are the oldest techniques used for the removal of arsenic in water. These techniques are widely used for removal of arsenic because of its ease and low cost [15,16]. In this study, commonly used ferric salts as ferric sulfate as a coagulant. In this method, dissolved arsenic in water gets converted to insoluble form hereafter get precipitated otherwise, adsorbed on the surface site of solid hydroxide and may be co-precipitate. Filtration/sedimentation process was used for the solid particles removal [1].

The objective of this study was to evaluate the influence of pH, contact time, and coagulant concentration on the removal efficiencies of As (III) and As (V) from water containing the low concentration of arsenic by ferric sulfate and further optimize the process for maximizing the removal. In the present investigation, the modeling study has been carried out using response surface methodology, a statistical experimental design and optimization tool, to predict and optimize the performance of chemical coagulation system. Response surface method provides vital information regarding the optimum conditions for each independent variable as well as studies the combined/interactive effect of these variables on the overall process. Further, these statistically designed experiments reduce the number of experiments while still considering the all individual and complex interaction between dependent variable on the overall process [17].This study was done to improve the As (III) and As (V) removal efficiencies present in synthetic and groundwater using ferric sulfate as coagulant using optimized process variables by coagulation/filtration method without any pre-oxidation step. Influence of important process variables such as pH, contact time, and coagulant dose on arsenic species removal efficiency was investigated and the optimized conditions thus obtained were applied to remove arsenic species from groundwater.

2. Materials and methods

2.1. Reagent

A stock solution of 1000 mg As (III)/L, and 1000 mg As (V)/L were procured from Inorganic Ventures, USA. Test water samples were prepared using regular tap water by appropriate dilution of the As (III) and As (V) stock solutions. All chemicals used in the study were of analytical grade. The synthetic coagulant stock of $10 gL^{-1}$ Fe (III) was prepared using anhydrous ferric sulfate $Fe_2(SO_4)_3$ as a source of the Fe(III) ions supplied by Merck.The stock solution of Fe(III) ions further diluted to obtain the desired concentrations in test water sample. Inductively coupled plasma-mass spectrometer (ICP-MS) (Perkin Elmer ICP mass spectrometer NEXLONTM300X) measured the total arsenic concentration. The pH meter (Eutech Instrument, pH510) was used to monitor the pH.

2.2. Characterization of test water and ground water sample

Table 1 lists the physiochemical properties of test water sample and groundwater sample collected from West Bengal; Kolkata employed in this study.5L high-density polyethylene container was used to store the groundwater sample and all experiments were conducted at room temperature. Standard methods [24] were used to estimate TDS, hardness, ammonium ions, sulfate ions, phosphate ions, nitrate ions, chloride ions and heavy metal concentrations.

Table 1

Characterization of test water sample and groundwater sample used in the experiment

Components	Unit	Test water sample	Groundwater sample	
			R_1	R_2
pH	----	7.52	6.75	7.08
Temperature	°C	23	24	22
Conductivity	μScm^{-1}	92.04	202.12	226.8
TDS	mgL^{-1}	24.42	90.12	78.08
Hardness	mgL^{-1}	22	165	169
Ammonium ions(NH_4^+)	mgL^{-1}	0	0.45	0.61
Sulfate ions(SO_4^{-2})	mgL^{-1}	3.02	10.42	4.24
Phosphate ions(PO_4^{-3})	mgL^{-1}	0.001	0.12	0.28
Nitrate ions(NO_3^+)	mgL^{-1}	3.04	8.16	9.02
Chloride ions(Cl^{-1})	mgL^{-1}	2.81	7.94	8.52
As	mgL^{-1}	0	0.083	0.091
Be	mgL^{-1}	0	0.002	0.001
Ca	mgL^{-1}	0.022	27.32	32.11

Cd	mgL^{-1}	0	0.002	0.002
Cr	mgL^{-1}	0	0.006	0.073
Cu	mgL^{-1}	0.001	0.021	0.017
Fe	mgL^{-1}	0.042	2.868	4.386
Mg	mgL^{-1}	0.012	8.321	9.524
Li	mgL^{-1}	0	0.005	0.003
Mo	mgL^{-1}	0	0.002	0.004
Mn	mgL^{-1}	0	0.035	0.029
Sb	mgL^{-1}	0	0.001	0.0004
Se	mgL^{-1}	0	0.003	0.004

[R1]Groundwater sample, WB, [R2]Groundwater sample, WB

2.3. Experimental procedure

The bench-scale Jar test apparatus with six beakers (Zexter Flocculator) was used to perform Coagulation/filtration experiments. Before the addition of coagulant in the beakers (1L) containing 100 µgL^{-1}As (III) and As (V) separately, pH of the solution was adjusted using 1N HCL and 1N NaOH. After rapid contact at 200 rpm, testing jars were allowed to settle for 30 min. The supernatant was drawn and filtered through 0.22 µm pore size membrane filter and stored for residual arsenic determination using inductively coupled plasma-mass spectrometer (ICP-MS).In **Table 2**, represents the operating conditions of ICP-MS instrument. All the experiments were performed in duplicate, and the arithmetic average of two duplicate experiments was considered for analysis.

Table 2

Operating conditions of ICP-MS

ICP-MS system	
RF Power	1150W
Sample Pump Rate	50 rpm
Auxiliary Gas Flow	0.5L/min
Nebulizer Gas Flow	0.5L/min
Plasma Gas Flow	15L/min
Nebulizer	Crossflow nebulizer
Spray Chamber	Concentric glass nebulizer

Plasma Mode	Axial
Argon gas	Ultra high purity
Autosampler	CETAC company
Sample amount	5mL
Instrument ID	iCAP 6300DUO

2.4. Sample preservation and analysis

After jar test experiments, samples were collected using syringe-filter of 0.22 μm size membrane filter. The samples were stored at 4°C in the refrigerator by adding 1-2 drops of trace metal grade 1N HNO_3 solution. Arsenic analyses of the stored samples were performed using ICP-MS.

2.5. Experimental Design

In the present work, a statistical general full factorial design was used for the design of experiments and process optimization for maximum arsenic [As (III) and As (V)] removal.Effect of coagulant dosage, contact time, and pH (independent variables) on the removal of arsenic (dependent variable) by coagulation/filtration was carried out to determine the optimal coagulant dose and reaction conditions by using factorial experimental design.The design consisted of 21 runs with pH concentrations (set at four different levels) of 4, 6, 8 and 10, time set at 10 and 20 minutes and three different concentration levels of Fe (III) are 10, 50 and 100mgL^{-1}.To obtain, the reproducibility of the data, duplicate experiments performed and the arithmetic average values with standard deviation reported here.Total 42 experiments were carried out in the chemical process for the As (III) and As (V) species removal in the test water sample by optimizing pH, contact time, and Fe (III) concentrations.The experiments designed by MINITAB 15 statistical software.In the developed model pH, contact time, and Fe (III) were the independent variables and %As (III) and %As (V) removal were the dependent variables[18].A regression analysis performed to estimate the predicted values as a second-order polynomial and is represented as

$$Y = \beta o + \sum_{i=1}^{\kappa} \beta_{bi} X_i + \sum_{j} \sum_{<i=2}^{k} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} X_i^2 \qquad (1)$$

Where y is the predicted response, β_o is a constant, β_{bi} the linear coefficient, β_{ii} the squared coefficient, β_{ij} the product-coefficient and n, is the number of factors. A quadratic model used including linear, squared and interaction terms. The relationship between independent variables and response was calculated using the second-order polynomial equation (Eq. 1).Analysis of variance (ANOVA) give the significant terms for each response. Table 3 showed the coded and uncoded values of three independent variables with responses. Actual values for three variable pH, contact time and Fe (III) with the comparison of experimental and predicted As (III) and As (V)

removal efficiencies were represented in **Table 3**. The total arsenic removal percentage (%) was calculated using following equation:

$$R\% = \frac{(Co-Cf)}{Co} \times 100 \qquad (2)$$

Where C_o and C_f are the initial and final concentration of As (III) and As (V) ($\mu g L^{-1}$) in the solution. The actual values obtained from the particular run were measured as response data, and predicted values were measured using the statistical model.

Table 3

Factorial design matrix for three test variables with coded and uncoded values with comparison of experimental and predicted % As (III) and As (V) removal efficiencies

pH	Contact Time (min)	Fe (III) (mgL⁻¹)	As (III) Obtained (%R.E)	As(III) Predicted (%R.E)	As (V) Obtained (%R.E)	As(V) Predicted (%R.E)
0(4)	1(20)	1(50)	61	65	67±2.3	72±5.3
1(6)	1(20)	0(10)	92	69	98±0.48	78±10.2
3(10)	0(10)	1(50)	91	94	95±2.34	95±0.93
3(10)	1(20)	2(100)	85	87	88±2.1	87±2.84
0(4)	1(20)	2(100)	78	76	81±1.8	77±5.1
2(8)	1(20)	0(10)	87	79	92±2.4	87±2.96
0(4)	0(10)	0(10)	32	39	48±4.5	63±9.11
2(8)	1(20)	1(50)	95	100	94±0.48	98±1.08
1(6)	1(20)	1(50)	90	93	97±1.02	92±4.06
1(6)	1(20)	2(100)	97	100	90±1.81	94±0.55
3(10)	0(10)	0(10)	34	80	38±7.5	89±0.78
3(10)	0(10)	2(100)	91	89	90±4.7	87±3.12
1(6)	0(10)	0(10)	83	73	90±1.62	85±7.15
0(4)	1(20)	0(10)	36	37	52±6.3	55±1.88
2(8)	0(10)	0(10)	83	86	91±4.75	94±4.09
0(4)	0(10)	1(50)	68	62	77±2.7	77±0.82
0(4)	0(10)	2(100)	64	69	78±5.92	79±4.67
1(6)	0(10)	2(100)	96	96	98±0.33	95±3.03
1(6)	0(10)	1(50)	91	93	96±3.6	96±0.74
3(10)	0(20)	1(50)	93	88	93±1.08	91±2.91
3(10)	0(20)	0(10)	65	70	82±5.92	83±2.55

[R.E]Removal efficiency, Brackets represent the uncoded value

3. Results and Discussion

3.1. Statistical Analysis of the results

The multiple regression analysis considering the full quadratic effect for the As (III) and As (V) removal yielded second order polynomials equations as follows

$$As(III)R.E = -102.946 + 44.276A + 0.314B + 0.938C - 2.54A^2 - 0.005C^2 - 0.142AB - 0.039AC + 0.010BC \qquad (3)$$

$$As(V)R.E = -18.5821 + 28.18A - 0.9657B + 0.6057C - 1.7002A^2 - 0.0033C^2 + 0.0289AB - 0.0328AC + 0.0064BC \qquad (4)$$

Where *A, B, C* are input pH, contact time and coagulant dose respectively of the chemical system. The R^2 and *predictive error sum of squares (PRESS)* checked the adequacies of the model. A model with large R^2 and low *PRESS* values are considered a good model [19]. The value of regression coefficient, indicating the fit of the developed models were found to be $R^2=0.9383$ and $R^2=0.9601$ for both As (III) and As (V). The *PRESS* value was found to be 1383.71 and 428.162 for As (III) and As (V) respectively. This indicated the correctness of developed regression model to predict the percentage removal of arsenic regarding independent variables, and also that model did not explain only about 6.17% and 3.99% of variations for As (III) and As (V) in the removal process. This shows that the model adequately represents the real relationships among the selected reaction factors. Further, R^2_{pred} (which represents the ability of the derived model to predict the output for unknown samples), was also found to be 0.7975 and 0.8694 for % As (III) and % As (V) removal respectively. The high R^2_{pred} for both models further justifies the developed models and its prediction capability. Fisher's variance ratio *F-value* is calculated as a ratio of mean square regression and mean square residual. It is the measure of variance in the data about the mean. ANOVA tables (**Table 4 & Table 5**) of the two models represents high *F-value* (20.90 and 33.53) and very low *P-value* (0.000) confirming the high significance of the models. The *P* values obtained from ANOVA were used as a tool to check the significance of each of the coefficients. These values are necessary to understand the pattern of mutual interactions between the test variables. The smaller the magnitude of *P*, more significant is the corresponding coefficient. The coefficient estimates for the As (III) and As (V) and the corresponding *P values* suggested that, among the parameters used in analysis C [*Fe (III) concentration*], second order interaction between A^2 (*pH*) & C^2 [*Fe (III) concentration*] and mutual interaction between *A x C* [pH and Fe (III)], all having *P* value < 0.005, were found to have significant effect on the response. Other interactions were found to be insignificant. The polynomial equations (3) & (4) and also AVONA **Table 4 and Table 5** implied that the pH of the medium had the greatest linear positive effect (*P = 0.00*) followed by the Fe (III) dose (on the As (III) and As (V) removal from the system). Further, the square effect of pH and Fe (III) doses had the positive effect on the removal. The negative interaction effect on pH and Fe (III) suggested that at the high levels of pH the removal efficiency starts to decrease. This can be studied from the

contour plots **Fig. 1-3**. The contact time had the negligible effect on the As (III) and As (V) removal. **Fig. 4(a-f)** shows the surface plots of the interactions of effect of pH, contact time, and Fe(III) concentration on % As (III) and % As (V) removal efficiencies to obtain maximum responses.

Table 4

Analysis of Variance (ANOVA) for response surface for % As (III) removal

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	8	6412.25	6412.25	801.53	20.90	0.000
Linear	3	3383.09	3620.53	1206.84	31.46	0.000
pH	1	2036.16	2783.69	2783.69	72.57	0.000
Time	1	23.14	4.12	4.12	0.11	0.749
Fe (III)	1	1323.80	642.79	642.79	16.76	0.002
Source	2	2775.11	2367.58	1183.79	30.86	0.000
pH*pH	1	2253.16	1947.94	1946.94	50.76	0.000
Fe (III)*Fe (III)	1	521.95	488.26	488.26	12.73	0.004
Interaction	3	254.05	254.05	84.68	2.21	0.145
pH*time	1	20.83	50.36	50.36	1.31	0.276
pH*Fe (III)	1	166.88	192.19	192.19	5.01	0.047
Time*Fe (III)	1	66.34	66.34	66.43	1.73	0.215
Residual error	11	421.95	421.95	38.36		
Total	19	6834.20				

R-sq=0.9383;R-sq(pred)=0.7975;R-sq(adj)=0.8934;S=6.19;PRESS=1383.71

DF=Degree of freedom, SS=Sum of squares

Table 5

Analysis of Variance (ANOVA) for response surface for % As (V) removal

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	8	3149.77	3149.71	393.72	33.53	0.000
Linear	3	1629.09	1921.85	640.62	54.55	0.000
pH	1	1147.95	1226.71	1226.71	104.46	0.000
Time	1	45.61	1.88	1.88	0.16	0.697
Fe (III)	1	435.53	523.12	523.12	44.55	0.000
Source	2	1303.92	1100.55	550.27	46.86	0.000

pH*pH	1	1010.95	853.80	853.80	72.71	0.000
Fe (III)*Fe (III)	1	292.97	280.83	4280.83	23.91	0.000
Interaction	3	216.77	216.77	72.26	6.15	0.010
pH*time	1	2.27	0.84	0.84	0.07	0.794
pH*Fe (III)	1	213.53	213.66	213.66	18.19	0.001
Time*Fe (III)	1	0.97	0.97	0.97	0.08	0.780
Residual error	11	129.18	129.18	11.74		
Total	19	3278.95				

R-Sq = 0.9606;R-Sq(pred) = 0.8694;R-Sq(adj) = 0.9320;S = 3.42685;PRESS = 428.162
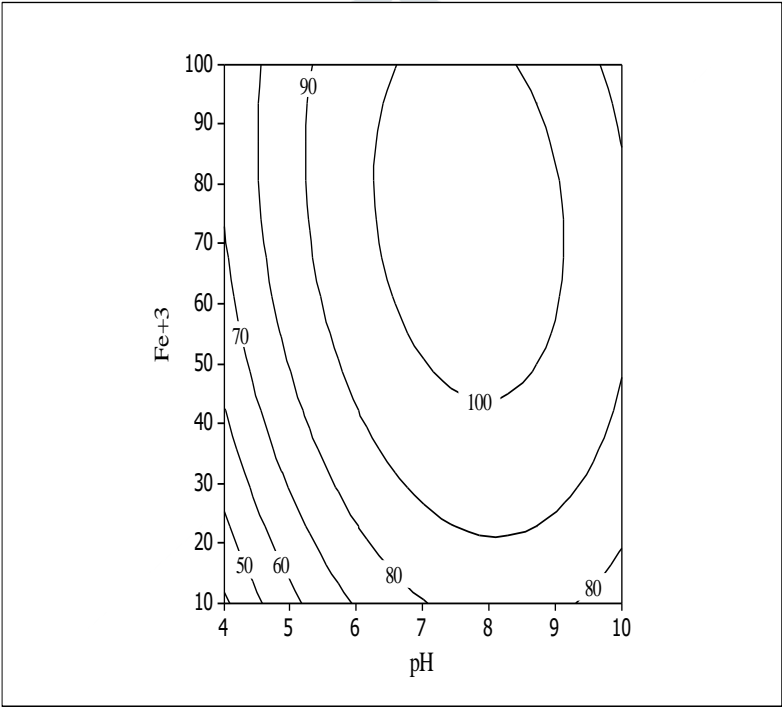
Fig.1(a). Response surface plot showing As (III) removal efficiency as a function of pH and

Fe (III) concentrations
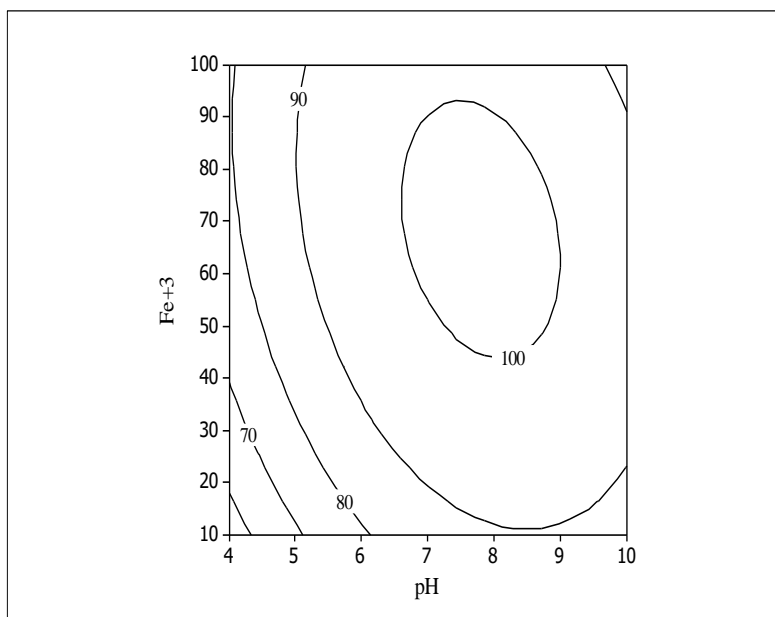
Fig.1(b). Response surface plot showing As (V) removal efficiency as a function of pH and

Fe (III) concentrations
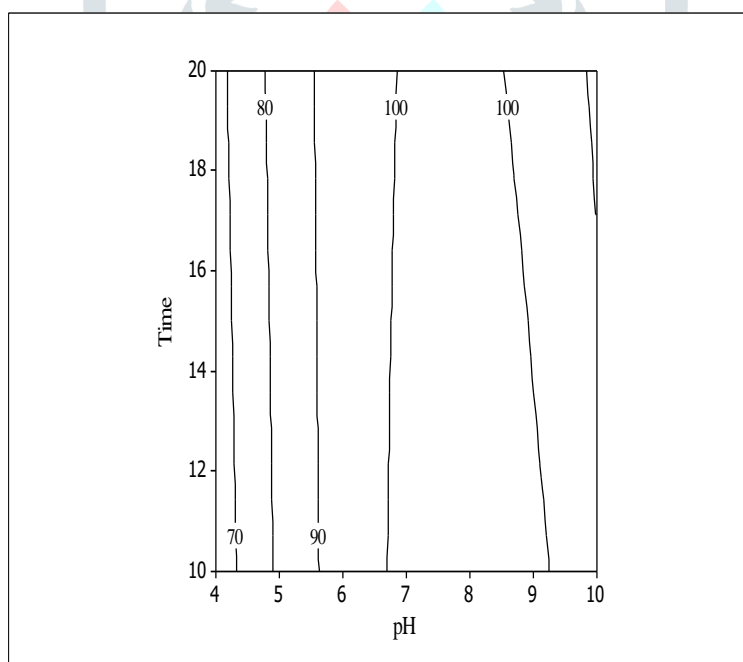
**Fig.2(a).** Response surface plot showing As (III) removal efficiency as a function of pH and contact time
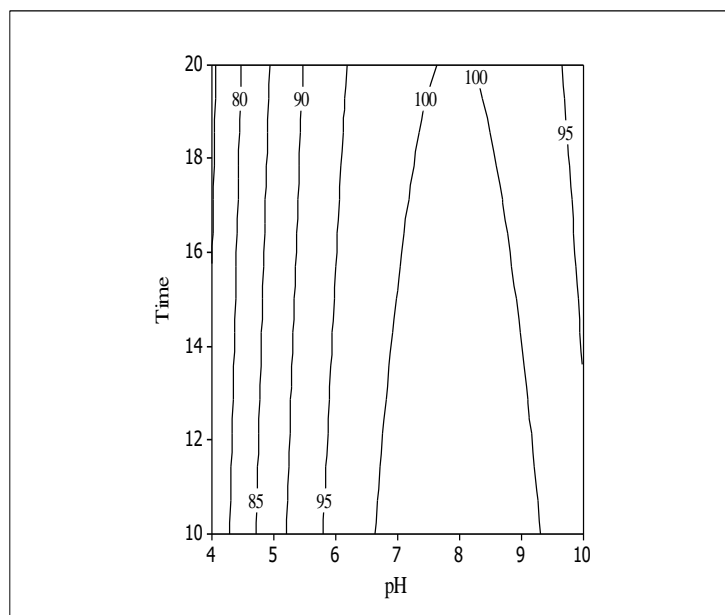
Fig. 2(b). Response surface plot showing As (V) removal efficiency as a function of pH and contact time

e

Fig.3(a). Response surface plot showing As (III) removal efficiency as a function of contact time and Fe (III) concentrations
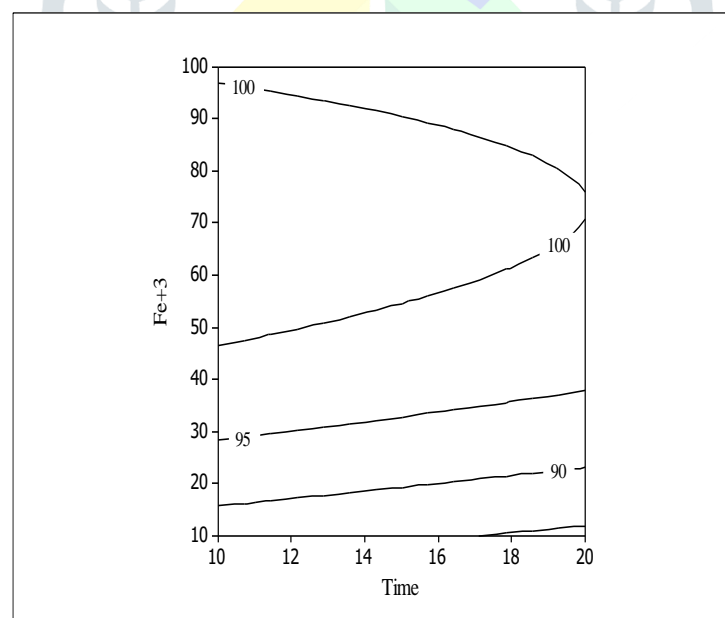
Fig. 3(b). Response surface plot showing As (V) removal efficiency as a function of contact time and Fe (III) concentrations
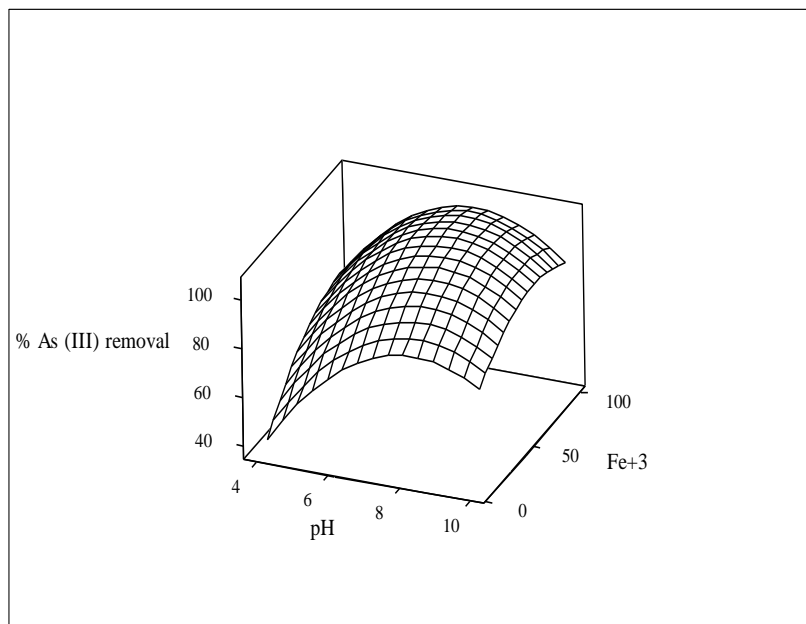
Fig. 4(a). Surface plot of % As (III) removal vs. pH and Fe (III) concentrations
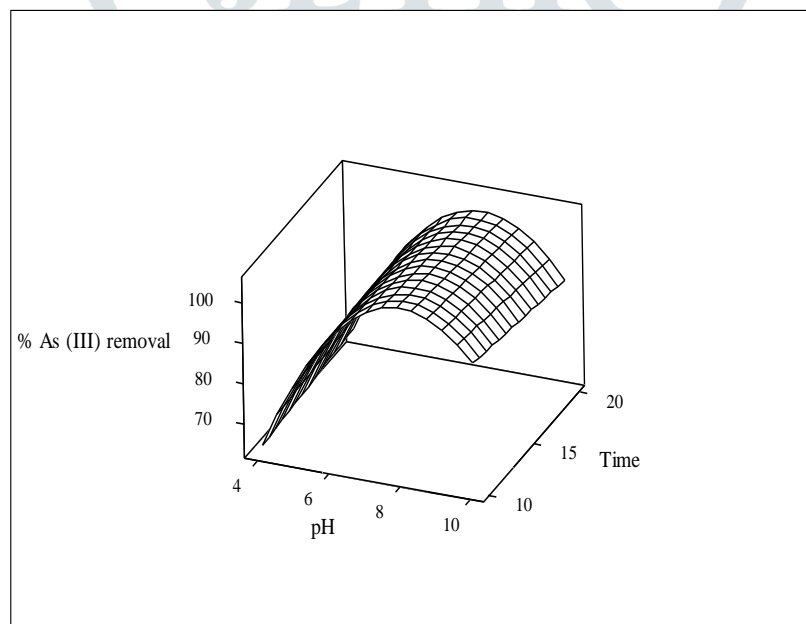
Fig. 4(b). Surface plot of % As (III) removal vs. pH and contact time
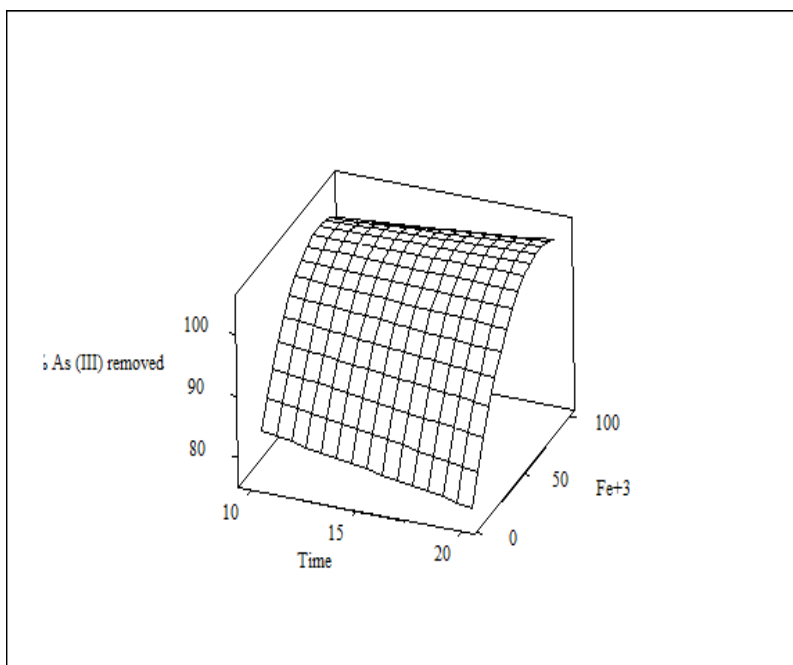
Fig.4(c). Surface plot of % As (III) removal vs. contact time and Fe (III) concentrations

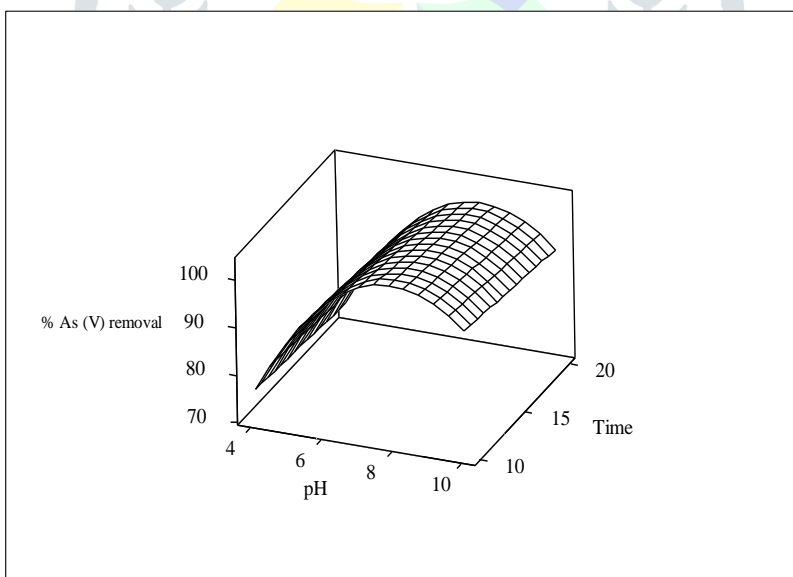**Fig.4(d).** Surface plot of % As (V) removal vs. pH and Fe (III) concentrations

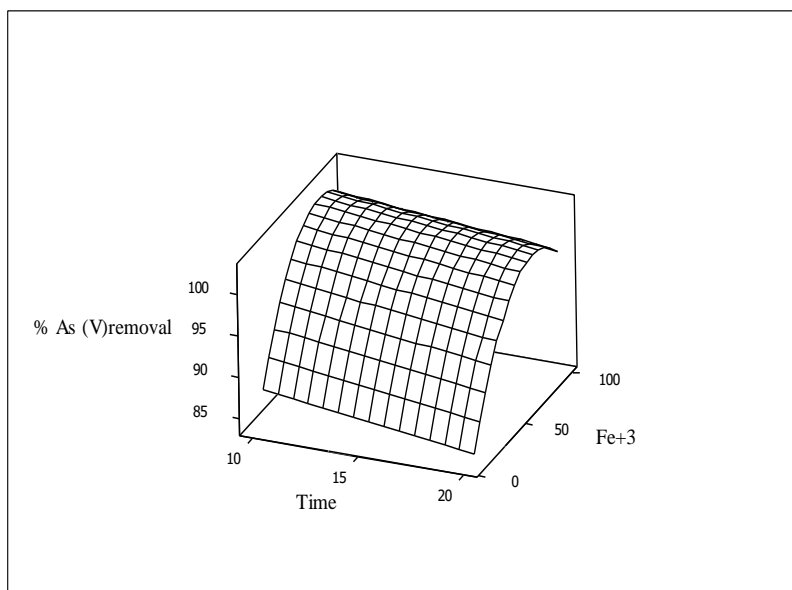**Fig.4(e).** Surface plot of % As (V) removal vs. pH and contact time

Fig.4(f). Surface plot of % As (V) removal vs. contact time and Fe (III) concentrations

To test the prediction capability of the fitted model developed using RSM an inverse range scaling was performed on all the experimental outputs (ICP output) to return predicted response (using RSM) for its subsequent comparison with experimental response (ICP output) [20]. **Fig. 5 & 6** shows a comparison between experimental values obtained as a result of ICP analysis and predicted response using RSM for As (III) and As (V) removal. **Fig.5 & 6** show the prediction capability of the developed model by using two lines: one line represented an ideal model wherein experimental data is equal to predicted data; while the other line obtained by plotting data fits obtained using developed RSM models and experimental responses of ICP.
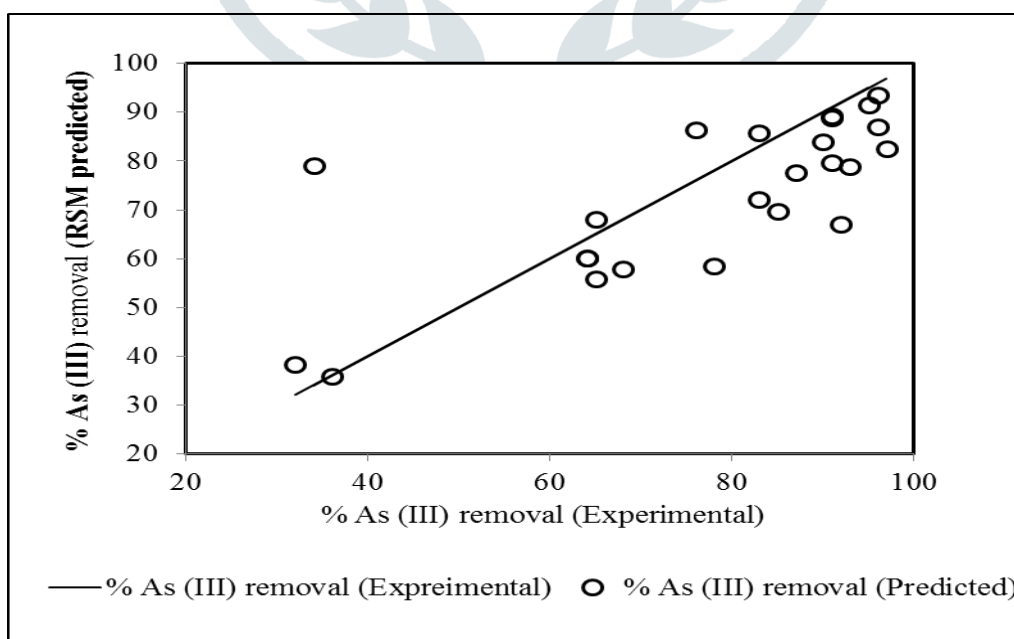

Fig.5. Experimental and predicted (Response Surface Methodology) % removal concentrations of As (III)
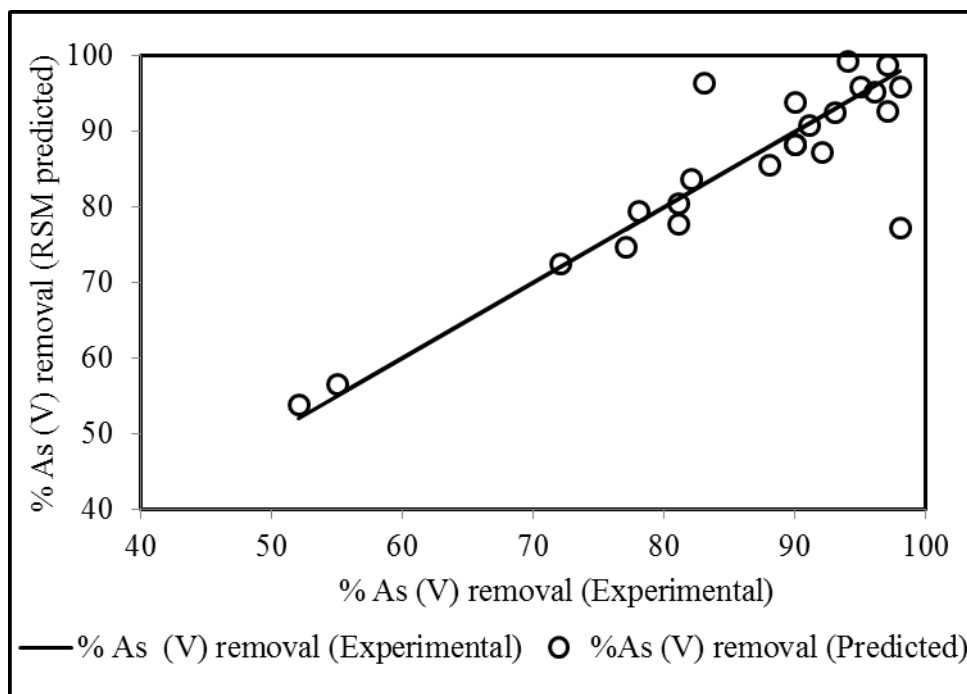
Fig.6. Experimental and predicted (Response Surface Methodology) % removal concentrations of As (V)

3.2. Optimization and Validation Experiments for As (III) and as (V) removal

The optimization was done to maximize the arsenic removal from the reactor system by controlling the independent parameters, *i.e.,* pH of the medium, contact time, and Fe (III) concentrations. **Fig. 1-3** shows the response surface curves for As (III) and As (V) removal by coagulation/filtration process. From the nature of contour plots, it is evident that interaction between the individual process variables is significant for pH and Fe (III) doses. The study of the contour plots reveals that the maximum removal of As (III) and As (V) was in between the pH range of 6.5-9.5.Among the variables, pH was the most significant parameter affecting the arsenic removal from the system and time was least significant parameter affecting the process. To maximize the As (III) and As (V) removal, numerical point prediction tool of MINITAB 15 was used to find the optimum values of test variables. During the optimization, the target set at 95% and the maximum set at 100%.The RSM predicted optimum conditions obtained were pH; 9 and 9.32, time; 10min and 15min and Fe (III) 30mgL^{-1} and 32mgL^{-1} respectively for As (III) and As (V) shown in **Table 6**. The composite desirability value *'D'* for the above condition was found to be very close to 1, 0.987 for As (III) and 0.998 for As (V) respectively.

Table 6

RSM, predicted optimum process parameters for maximum As (III) and As (V) removal

Parameters	Units	Optimum value predicted		Removal efficiencies
For 100 µgL^{-1} initial As(III) and As(V)		AS(III)	As(V)	
pH	----	9	9.32	As(III):>=95%
Time	min	10	15.47	As(V): >=95%
Fe (III)	mgL^{-1}	29-30	32	

To test the effectiveness and validity of the optimized conditions, additional validation experiments were performed. The % As (III) and % As (V) removal was monitored in five sets of experiments were performed on above sets of the conditions. Average of measured and predicted As (III) removal efficiencies were 89.46 % and 95.52 % with standard deviation of 3.23 whereas for As (V), an average of measured and predicted removal efficiencies were 91.62 % and 95.21 % with standard deviation of 2.4 respectively. **Table 7** presented the results of validation experiments. The results showed that experimental results were in good agreements with the response function predicted results. So that quadratic model can be effectively used to optimize the operating process variable (i.e. pH, contact time and initial ferric ions concentration) in the treatment of groundwater having fixed concentration of Arsenic.

Table 7

Validation experiments result using optimal process variables for As (III) and As (V) removal

Input parameters(Optimized)								As (III) and As (V) Removal efficiency (%)			
Inlet Conc. (µgL^{-1})		pH		Time (min)		Fe(III) (mgL^{-1})		Experimental		Predicted	
As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
97±1	95±1	9±0.2	9.3±0.2	10	15	30±2	32±2	85	90.71	95.52	95.21
97±1	95±1	9±0.2	9.3±0.2	10	15	30±2	32±2	87.45	95.21	95.52	95.21
97±1	95±1	9±0.2	9.3±0.2	10	15	30±2	32±2	90.05	92.59	95.52	95.21
97±1	95±1	9±0.2	9.3±0.2	10	15	30±2	32±2	92.65	90.75	95.52	95.21
97±1	95±1	9±0.2	9.3±0.2	10	15	30±2	32±2	92.16	88.84	95.52	95.21

4. Application of optimized condition for treatment of groundwater

The developed model and the optimized conditions were used to check its applicability to the groundwater sample. Similar experiments were done with the groundwater samples containing arsenic from West Bengal (WB) under the optimum process condition (determined for synthetic test water contaminated with $100\mu gL^{-1}$ As (III) and As (V) respectively).**Table 1** represented the chemical composition and properties of groundwater. Arsenic concentrations present [contain As (V) only] in both the groundwater samples were $83\mu gL^{-1}$ and $91\mu gL^{-1}$ determined by HPLC-ICP-MS (High-performance liquid chromatography-Inductively couples plasma-mass spectrometer). The percentage removal of arsenic and other heavy metals were illustrated in **Fig.5.** Similar, environmental, geometric and hydrodynamic conditions indicate that an experimental As (III) and As (V) removal from synthetic water which is very close to that obtained response for ground waters samples contaminated with Arsenic. This indicates that about 80-85% arsenic was removed in case of groundwater. Ground water samples also contain other ions and heavy metals which might affect the arsenic removal efficiency to some extent.The background ions such as sulfate and chloride negligibly affect the arsenic removal. Whereas, removal performance of arsenic was significantly inhibited by phosphate and nitrate [21,22].It illustrates the fact that if similar geometric, environmental and hydrodynamic are maintained, the similar results can be obtained for water matrix contaminated with arsenic. As (III) and As (V) removal obtained in the present investigation involving single step only without any pre-oxidation step.
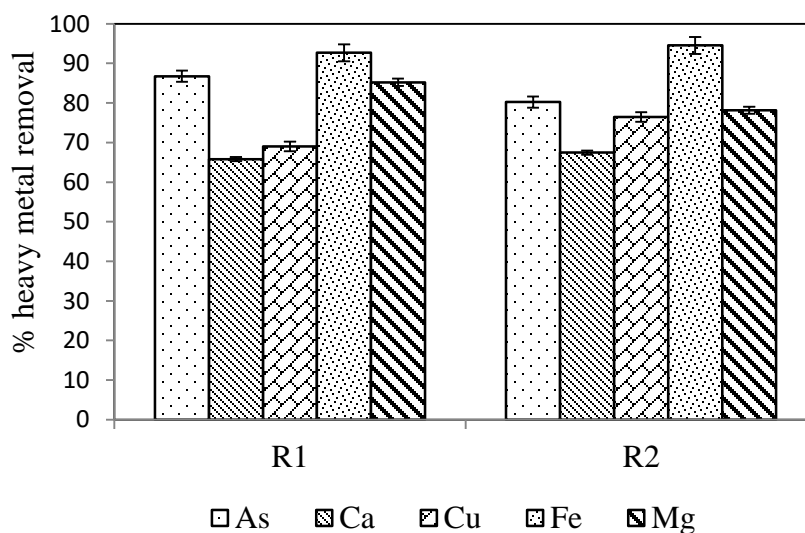

Fig.5. %Arsenic As (V) removal and other heavy metals for the groundwater samples (R1 and R2) determined using optimal conditions

5. Conclusion

A design was formulated using general full factorial design and analyzed using response surface methodology to evaluate the effect of initial solution pH, contact time, and initial Fe (III) concentration on the removal efficiencies of As (III) and As (V) species from test water sample and groundwater sample using ferric sulfate as a coagulant using chemical coagulation and filtration process.This study was evaluated the impact of important independent variables on the As (III) and As (V) removal efficiencies. Factorial design method was employed to determine optimal values of operating variable by reducing the required number of experiments. Experimental results showed that the optimal pH values for effective As (III) and As (V) removal having constant initial As (III) and As (V) of $100\mu gL^{-1}$ was obtained to be 9 and 9.3 for As (III) and As (V) respectively. Results revealed that contact time cannot affect the As(III) and As(V) removal efficiencies remarkably. There was no significant impact of contact time on percentage arsenic species removal. Whereas, optimal values of ferric ions Fe (III) for highest As (III) and As (V) species removal was found to be $30mgL^{-1}$ and $32mgL^{-1}$ respectively by conducting experimental runs. From the study, it was confirmed that ferric sulfate (as a source of ferric ions) was effective coagulant for the maximum As (III) and As (V) species removal is having low initial As (III) and As (V) concentration ($100\mu gL^{-1}$).

References

[1]M.B.Baskan,P.A.Aysegul,Statistical experiment design approach for arsenic removal by coagulation process using aluminum sulfate,Desalination.254(2010)42–48.

[2]M.Kobya,E.Sik,M.S.Oncel,E.Demirbas,A.Y.Goren,A.Akyol,Y,Yildirim,Removal of low concentration of As (V) from groundwater using an air injected electrocoagulation reactor with iron ball anodes: RSM modeling and optimization.Digital proceeding of The ICOEST 2013-Cappadocia,2013.

[3]M.V.B.Krishna,K.Chandrasekaran,D.Karunasagar,J.Arunachalam,A combined treatment approach using Fenton's reagent and zero-valent iron for the removal of arsenic from drinking water,Journal of Hazardous Materials B. 84(2001)229–240.

[4]P.Mondal,C.B.Majumder,B,Mohanty,Laboratory-based approaches for arsenic remediation from contaminated water: Recent developments,Journal of Hazardous Materials B.137(2006) 464–479.

[5]M.A.Rahman,B.Hogan,E.Duncan,C.Doyle,R.Krassoi,M.M,Rahman,R.Naidu,R.P.Lim, W.Maher,C.Hassler,Toxicity of arsenic species to three freshwater organisms and biotransformation of inorganic arsenic by freshwater phytoplankton(Chlorella sp. CE-35), Ecotoxicology and Environmental Safety.106(2014)126–135.

[6]A.Hussam,A.K.Munir,A simple and effective arsenic filter based on composite iron matrix: Development and deployment studies for groundwater of Bangladesh,Journal of environmental science and health part A.42(2007)1869–1878.

[7]WHO,Guideline for drinking water quality. World Health Organization, Geneva,2001. P-41.

[8]K.T.Lim,M.Y.Shukor,H.Wasoh,Physical, Chemical and Biological Methods for the removal of arsenic compounds.Biomed Research International,2014.doi.org/10.1155/2014/503784.

[9]T.S.Y.Choong,T.G.Chuah,Y,Robiah,K.F.L.Gregory,I.Azni,Arsenic toxicity,health hazards and removal techniques from water: An overview,Desalination.217(2007)139–166.

[10]S.V.Jadhav,E.Bringas,G.D.Yadav,V.K.Rathod,I.Ortiz,K.V.Marathe,Arsenic and fluoride contaminated ground waters: A review of current technologies for contaminants removal, Journal of Environmental Management.162(2015)306-325.

[11]M.B.Baskan,A.Pala,Determination of arsenic removal efficiency by ferric ions using response surface methodology,Journal of Hazardous Materials.166(2009)796–801.

[12]I.Villaescusa,J.C.Bollinger,Arsenic in drinking water: sources, occurrence and health effects (a review),Reviews in Environmental Science and Biotechnology.7(2008)307–323.

[13]S.Chakraborty,M.O.Alam,T.Bhattacharya,Y.N.Singh,Arsenic Accumulation in Food Crops:A Potential Threat in Bengal Delta Plain,Water Quality, Exposure and Health.6(2014)233–246.

[14]O.S.V.Ehrenstein,D.N.G.Mazumder,M.H.Smith,N.Ghosh,Y.Yuan,G.Windham,A.Ghosh,R.Haque,S.Lahiri ,D.Kalman,S.Das,A.H.Smith,Pregnancy outcomes, Infant Mortality,and Arsenic in Drinking Water in West Bengal, India,American Journal of Epidemiology. 163(2006).DOI: 10.1093/aje/kwj089.

[15]C.C.Mólgora,A.M.Domínguez,E.M.Avila,P.Drogui,G.Buelna,Removal of arsenic from drinking water: A comparative study between electrocoagulation-microfiltration and chemical coagulation-microfiltration processes,Separation and Purification Technology.118(2013)645–651.

[16]D.Lakshmanan,D.A.Clifford,G.Samanta,Comparative study of arsenic removal by iron using electrocoagulation and chemical coagulation,Water research.44(2010)5641-5652.

[17]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, Environmental Technology.33(2012)159–165.

[18]M.B.Kasiri,H.Aleboyeh,A.Aleboyeh,Modeling and Optimization of Heterogeneous Photo-Fenton Process with Response Surface Methodology and Artificial Neural Networks, Environmental Science and Technology.42(2008)7970 -7975.

[19]D.C.Montgomery,Design and Analysis of Experiments.5th Edition, Wiley, New York.2011

[20]S.C.Deshmukh,J.Senthilnath,R.M.Dixit,S.N.Malik,R.A.Pandey,A.N.Vaidya,S.N.Omkar,S.N.Mudliar,Comparison of Radial Basis Function Neural Network and Response Surface Methodology for Predicting Performance of Bio-filter Treating Toluene,Journal of Software Engineering and Applications,5(2012)595-603.

[21]X.Meng,S.Bang,G.P.Korfiatism,Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride,Water Research.34(2000)1255-1261.

[22]V.Tanboonchuya,N.Grisdanurak,C.H.Liaoc,Background species effect on aqueous　　arsenic removal by nano zero-valent iron using fractional factorial design,Journal of Hazardous　　Materials.205(2012)40– 46.

[23]M.M.Rahman,B.K.Mandal,T.R.Chowdhury,M.K.Sengupta,U.K.Chowdhur,D.Lodh,
C.Chanda,G.K.Basu,S.C.Mukherjee,K.C.Saha,D.Chakraborti,Arsenic Groundwater Contamination and Sufferings of People in North 24-Parganas, One of the Nine Arsenic Affected Districts of West Bengal, India,Journal of Environmental Science and Health, Part A—Toxic/Hazardous Substances & Environmental Engineering.38(2003)25–59.

[24]Standard Methods for the examination of water and wastewater, 21st edition.2005.