

Article

Optimization of Antimony Removal by Coagulation-Flocculation-Sedimentation Process Using Response Surface Methodology

Muhammad Ali Inam ^{1,*}, Rizwan Khan ², Ick Tae Yeom ³, Abdul Salam Buller ⁴, Muhammad Akram ⁵ and Muhammad Waleed Inam ⁶

¹ Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Sciences and Technology (NUST) H-12 Campus, Islamabad 44000, Pakistan

² Department of Chemical Engineering, Quaid-e-Awam University of Engineering, Science and Technology (QUEST), Nawabshah Sindh 67480, Pakistan; rizwansoomro@quest.edu.pk

³ Graduate School of Water Resources, Sungkyunkwan University (SKKU), 2066, Suwon 16419, Korea; yeom@skku.edu

⁴ Department of Civil Engineering, Quaid-e-Awam University of Engineering, Science and Technology (QUEST), Campus Larkana, Sindh 77110, Pakistan; buller.salam@quest.edu.pk

⁵ Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Qingdao 266200, China; m.akramsathio@mail.sdu.edu.cn

⁶ Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan; mwaleedinam@gmail.com

* Correspondence: ainam@iese.nust.edu.pk; Tel.: +92-51-9085-4303

Abstract: Coprecipitation-adsorption plays a significant role during coagulation-flocculation-sedimentation (C/F/S) of antimony (Sb) in water. This work uses a Box–Behnken statistical experiment design (BBD) and response surface methodology (RSM) to investigate the effects of major operating variables such as initial Sb(III, V) concentration (100–1000 µg/L), ferric chloride (FC) dose (5–50 mg/L), and pH (4–10) on redox Sb species. Experimental data of Sb(III, V) removal were used to determine response function coefficients. The model response value (Sb removal) showed good agreement with the experimental results. FC showed promising coagulation behavior of both Sb species under optimum pH (6.5–7.5) due to its high affinity towards Sb species and low residual Fe concentration. However, a high dose of 50 mg/L of FC is required for the maximum (88–93%) removal of Sb(V), but also for the highest (92–98%) removal of low initial concentrations of Sb(III). Furthermore, BBD and RSM were found to be reliable and feasible for determining the optimum conditions for Sb removal from environmental water samples by a C/F/S process. This work may contribute to a better understanding and prediction of the C/F/S behavior of Sb(III, V) species in aqueous environments, to reduce potential risks to humans.

Keywords: antimony; Box–Behnken design; coagulation-flocculation-sedimentation; ferric chloride; water treatment



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1. Introduction

Antimony (Sb) has been used extensively worldwide in various commercial applications, including the manufacture of chemicals, plastics, batteries, ceramics, semiconductor materials, and flame retardants [1,2]. As a result, inorganic antimony (trivalent antimony (Sb[III]) and pentavalent antimony (Sb[V])) shows elevated concentrations in natural water bodies in different parts of the world. For example, Sb concentrations of 239, 6384, and 157 µg/L have been found in Stampede and Slate Creek watersheds (Alaska, USA), rivers around antimony mines in the Xikuangshan area (Hunan Province, China), and lakes in the South East region (Sindh, Pakistan), respectively [3–5]. Oral uptake of water-soluble Sb into the human body imparts toxic health impacts, including abdominal cramps, cardiac toxicity, vomiting, and diarrhea [6]. Therefore, Sb is considered to be a pollutant

of high priority interest by the United States Environmental Protection Agency (USEPA) and the European Union (EU) [7]. To protect human health and the environment, the USEPA (6 µg/L), EU (10 µg/L), World Health Organization (WHO) (5 µg/L), South Korea (20 µg/L), and Pakistan (5 µg/L) have set regulatory standards for Sb in drinking water [8–10].

Antimony is an emerging pollutant. It exists as Sb(III) under anoxic conditions and Sb(V) in aerobic waters, leading to long and persistent contamination when it is released into an aqueous environment [11]. Several treatment techniques including membrane separation, coagulation, adsorption, ion exchange, phytoremediation, and electrochemical methods have been extensively applied for the removal of Sb from drinking water [12]. However, coagulation-flocculation-sedimentation (C/F/S) processes are still favored by the drinking water industry. They have been identified as cost-effective and efficient treatment technologies to remove several heavy metals from water [13]. During the removal process, coagulant type and dosage, pH, and initial contaminant loading are key factors in determining the overall C/F/S performance of heavy metals in water. For instance, extensively used commercial coagulants such as ferric chloride (FC) and ferric sulfate (FS) have demonstrated more efficient Sb removal than aluminum-based coagulants [12,13]. High Sb(III) removal has been previously reported over a broad pH range (4–10). However, a significant decline in Sb(V) removal at alkaline pH conditions has been observed owing to a significant decrease in Fe solubility [14–16]. Higher FC coagulant doses in various aqueous environments lead to greater removal of both Sb(III, V) species [11,12,15]. The initial Sb loading affects the overall C/F/S performance, with higher removal for solutions with higher initial Sb(III, V) concentration than those with lower contaminant loading [11,12]. The treatment of Sb-rich water has been addressed in a number of studies [11,12,14–17] using the C/F/S process. However, previous studies are limited to “one-factor-at-a-time” experiments to determine the coagulation behavior of Sb species in water. Studies that comprehensively determine the interactive effect of major operating parameters on Sb removal involved in the coagulation process are insufficient. Therefore, it is essential to explore an experimental approach for simulating Sb removal by C/F/S.

Toxic Sb species pose substantial threats to human health and the environment. Therefore, their removal from drinking water supplies by C/F/S is of essential importance. Furthermore, it is necessary to optimize the treatment efficiency of the C/F/S process by taking into consideration the concentration and characteristics of Sb species in order to achieve high Sb coagulation efficiency. The jar test procedure has been extensively employed to optimize Sb removal performance by a C/F/S process [11,12,14–18]. This classical approach is also referred to as the one-factor-at-a-time method, changing the level of one factor while keeping other factors constant. However, it is usually incapable of considering the interactive behavior of various operating factors. Thus, it is an insignificant approach to determine optimum conditions [19–21]. To overcome such a problem, numerous statistical and mathematical models have been developed for analyzing and optimizing experimental operating factors. For such a purpose, the Box–Behnken statistical experiment design (BBD) is a classical response surface methodology (RSM) used for modeling and analyzing experimental data [22]. The RSM is an empirical statistical technique for designing experiments, building models, evaluating the effect of variables, and searching for the optimum conditions of variables to predict targeted responses. It uses regression analysis of experimental data to solve a system of equations to obtain a single function response (the dependent variable examined), which can be graphed as a response surface [23–25]. It does not require a large number of runs. It does not require too many levels of independent variables either [26].

Up to date, a limited number of research studies have been conducted to investigate the coagulation process in drinking water using the RSM technique. Previously, the RSM technique has been applied to optimize the coagulation conditions for arsenic (As) removal using various coagulants [25,27]. The interaction of As and natural organic matter has also been investigated using RSM. The model has been validated with real groundwater samples containing both As and organic matter [28]. To the best of our knowledge, studies that simulate the C/F/S performance of Sb by FC coagulant using RSM have not been reported yet. It is essential to systematically investigate the removal performance of Sb by the C/F/S process using a mathematical modeling approach.

Accordingly, the aim of the present study was to explore the removal capability of redox Sb(III, V) species from aqueous solutions by coprecipitation-adsorption using FC as a coagulant. A Box–Behnken experimental design was used to investigate the effects of various coagulation factors such as pH, FC coagulant doses, and initial Sb(III, V) concentration on the removal efficiency of Sb and to find desirable operating conditions for achieving the maximum Sb removal. Secondly, the adequacy of the model and the reliability of statistical analysis with various experimental data points were determined by comparing the experimental and predicted response values of Sb removal efficiencies. Lastly, observed and modeled removal response values for real water matrices were compared to further illustrate the suitability of the model for Sb removal from drinking water using the C/F/S process.

2. Materials and Methods

2.1. Reagents and Stock Solutions Preparation

Potassium hexahydro-antimonate ($\text{KSb}(\text{OH})_6$), antimony (III) oxide (Sb_2O_3), and humic acid were purchased from Sigma Aldrich (St. Louis, MO, USA). Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), potassium chloride (KCl), sodium sulfate (Na_2SO_4), sodium bicarbonate (NaHCO_3), nitric acid (HNO_3), magnesium chloride (MgCl_2), hydrochloric acid (HCl), and sodium hydroxide were procured from Samchun (Samchun pure Chemicals Co., Ltd., Pyeongteak-si, Korea). Deionized (DI) water was produced in the laboratory using a water purification system (Milli-Q, Millipore Co., Bedford, MA, USA). Stock solutions of Sb(V) and Sb(III) were prepared at 1000 mg/L by dissolving $\text{KSb}(\text{OH})_6$ and Sb_2O_3 in DI water and 2M HCl solution, respectively, for further dilution to obtain solutions with the desired Sb(III, V) concentrations. A stock solution of Fe(III) was prepared at 500–5000 mg/L by dissolving $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in DI water for further dilution to obtain the desired Fe(III) concentrations for a particular experimental run. A stock solution of model organic matter was prepared at 0.1 g C/L by dissolving humic acid in DI water following a similar procedure as described in our previous studies [14,17,18]. In order to avoid the interference of unwanted contaminants, all glass vessels and glassware were initially washed with 15% HNO_3 solution followed by rinsing with DI water.

2.2. Experimental Procedure

Prior to the coagulation experiment, 100 mL of synthetic water was added in a 250 mL beaker. The predetermined amount of FC coagulant was added and a small quantity of 0.1 M HCl and 0.1 M NaOH solution was added to adjust the pH. A jar tester apparatus with six beakers (Model: SJ-10, Young Hana Tech Co., Ltd., Gyeongsangbuk-Do, Korea) was used to conduct the C/F/S experiments at a temperature of $25 \pm 1^\circ\text{C}$. C/F/S experimental conditions included a rapid coagulation at 140 rpm for 3 min, a flocculation at 40 rpm for 20 min, a sedimentation for 30 min, and a filtration using a $0.45\ \mu\text{m}$ glass fiber filter [14–18]. Aliquots (50 mL) were collected after the filtration process and stored in the dark at 4°C for further analysis.

2.3. Analytical Methods

A pH meter (HACH: HQ40d Portable pH, Conductivity, oxidation reduction potential (ORP) and ion selective electrode (ISE) Multi-Parameter Meter, Loveland, CO, USA) was used to measure solution pH after calibration with buffer solutions of 4.01, 7.00, and 10.01 at 25 °C. A popular statistical modeling software Design Expert (Version 7.0.0, Stat-Ease Inc., Minneapolis, MN, USA) was used for the experimental design, co-efficient determination, statistical data analysis, and response graph plotting. An inductively coupled plasma optical emission spectrometry (ICP-OES: Model Varian, Agilent technologies, Santa Clara, CA, USA) was used to analyze the residual Sb concentration from aqueous matrices. All experiments were performed in duplicate and average values were reported.

2.4. Response Surface Methodology

In order to explore the interactions of various major operating factors on antimony removal by the coagulation process and further optimize coagulation conditions, the Box–Behnken experimental design method [24] was used in this study. The following three major independent factors were chosen for the experimental design: initial Sb(III, V) concentration (A: 100–1000 µg/L), FC coagulant dose (B: 5–50 mg/L), and pH (C: 4–10). This BBD design was used to investigate all three factors at three equally spaced coded levels designated as −1 (low), 0 (middle), and +1 (high) levels of each variable. Actual values of coded levels of each factor are presented in Table 1.

Table 1. Levels of each independent factor for Box–Behnken.

Factors	Units	Symbol	Coded Levels		
			−1	0	+1
Initial Sb(III, V) concentration	µg/L	A	100	550	1000
Ferric chloride (FC) dose	mg/L	B	5	27.5	50
pH	-	C	4	7	10

The Box–Behnken statistical design provided 17 different combinations of experiments in a randomized order to minimize the effects of uncontrolled variables on responses, with the central point of the model repeated five times in order to quantify the error. Experimental data points of the three independent variables for BBD are shown in Table 2. Responses were modeled as an empirical second order polynomial equation in the form presented in Equation (1):

$$Y = f(x) = \beta_0 + \sum_{i=1}^k (\beta_i x_i) + \sum_{i=1}^k x_i \sum_{j=i+1}^k (\beta_{ij} x_i x_j) + \sum_{i=1}^k (\beta_{ii} x_i^2) \quad (1)$$

where Y was the predicted response (Sb(III, V) removal); k was the number of factors; x_i and x_j were coded values of factors that influenced the predicted response Y; β_0 was the model coefficient; and β_i , β_{ii} , and β_{ij} were linear, square, and interactive effects, respectively, of various independent variables.

Regression analysis was performed for experimental data thus obtained using Design Expert software. The statistical significance of the model was accessed by analysis of variance (ANOVA) in Design Expert, which was also used to depict the 3D response surface for the validation of experimental data by comparing it with predicted values. Furthermore, the model was used to find the maximum removal of response variable (Sb(III, V) removal) during the coagulation process under similar experimental conditions in an aqueous environment.

Table 2. Experimental data points used in Box–Behnken experimental design.

Experimental Run	Initial Sb(III, V) Concentration ($\mu\text{g/L}$)	FC Dose (mg/L)	pH
1	100	27.5	4
2	550	27.5	7
3	550	5	4
4	1000	5	7
5	100	27.5	10
6	100	50	7
7	1000	27.5	4
8	550	5	10
9	550	27.5	7
10	100	5	7
11	1000	27.5	10
12	550	27.5	7
13	550	27.5	7
14	550	27.5	7
15	550	50	4
16	1000	50	7
17	550	50	10

2.5. Environmental Water Samples

In order to extend the application of BBD for antimony removal, four different environmental water samples were examined in this study. Three water samples (freshwater, groundwater, and seawater) were synthetically prepared in DI water in accordance with our previous study [29], while a tap water sample was collected from Sungkyunkwan University, Korea. An amount of 1000 $\mu\text{g/L}$ Sb(III, V) was added into all water samples to understand the coagulation behavior of antimony in a natural water environment. Actual experimental values were compared with modeled values to determine the accuracy of the model. Table 3 presents detailed characteristics of various environmental water samples.

Table 3. Characteristics of synthetic and natural water samples.

Parameter	Fresh Water	Ground Water	Sea Water	Tap Water
pH	6.90	7.51	7.90	7.02
Conductivity ($\mu\text{S/cm}$)	119	965	26100	82.42
Ionic Strength (mM/L)	0.79	12.09	381	0.002
TOC (mg/L)	6	0	5.51	-
HCO_3^- ($\text{mg CaCO}_3/\text{L}$)	12	153	60	>80
PO_4 (mg/L)	0.64	0	0	-
Na^+ (mg/L)	0	158	6350	0.31
K^+ (mg/L)	1.20	8.59	230	0.06
Mg^{2+} (mg/L)	3.49	27.40	815	0.14
Ca^{2+} (mg/L)	1.50	49.50	245	0.81
Cl^- (mg/L)	6.61	141	10500	0.28
SO_4^{2-} (mg/L)	0	20	950	-
Sb (mg/L) *	1 *	1 *	1 *	1 *

* indicates Sb(III, V) solutions were spiked in water samples.

3. Results and Discussions

3.1. Identifying Best Response Function for Experimental Data

The removal of Sb(III, V) from drinking water following the coprecipitation-adsorption mechanism was investigated by the C/F/S process using FC coagulant. RSM was applied to model the experimental data obtained from 3-factor BBD, including initial Sb(III, V) concentration, FC dose and pH as process variables [17]. Experimental and predicted response variables (Sb(III)/Sb(V) removal) using FC as a coagulant are presented in Table 4. Different response functions such as linear, interactive, quadratic, and cubic models were generated and correlated with experimental data for regression analysis. To decide the adequacy of each model to represent Sb(III)/Sb(V) removal by FC, model summary statistics were conducted. The results are presented in Table 5. For both response variables (Sb(III) and Sb(V) removal), the quadratic model was selected for further analysis as it fitted the experimental data the best with the lowest standard deviations, the highest correlation coefficients, adjusted R^2 , predicted R^2 values, and the lowest p values without the aliasing, which occurred in the cubic model where sufficient points in the estimation of model coefficients were not available. The second order polynomial response equation was fitted for Sb(III) and Sb(V) removal to obtain the model constant, three linear, interactive, and quadratic effects, as indicated in Equation (1). Both response functions with determined coefficients for Sb(III) and Sb(V) removal in terms of coded factors are presented in Equations (2) and (3). Coefficients A, B, and C represent initial Sb(III, V) concentration ($\mu\text{g/L}$), FC dose (mg/L), and pH, respectively.

$$\text{Sb(III) removal} = 86.30 + 5.32A + 17.54B + 6.57C + 0.40AB - 1.67AC - 0.16BC - 2.25A^2 - 6.13B^2 - 8.49C^2 \quad (2)$$

$$\text{Sb(V) removal} = 85.82 + 2.71A + 9.85B - 4.47C - 3.68AB - 0.49AC - 0.76BC - 4.20A^2 - 3.05B^2 - 76.89C^2 \quad (3)$$

Table 4. Comparison of observed and predicted antimony removal efficiency.

Experiment No.	Removal Efficiency (%)			
	Sb(III)		Sb(V)	
	Observed	Predicted	Observed	Predicted
1	56.47	62.01	8.48	5.99
2	86.79	86.30	85.36	85.82
3	49.26	47.41	6.89	0
4	66.42	65.29	69.91	75.11
5	81.47	78.49	0	0
6	88.61	89.74	94.58	89.38
7	73.12	75.98	10.43	12.39
8	54.21	60.88	0	0
9	85.48	86.30	86.09	85.82
10	59.15	55.46	52.68	62.33
11	91.32	85.79	0	2.49
12	87.18	86.30	85.48	85.82
13	86.47	86.30	86.92	85.82
14	85.59	86.30	85.23	85.82
15	89.49	82.82	13.26	20.95
16	97.50	100.0	97.11	87.46
17	93.78	95.63	3.34	10.50

Table 5. Model summary statistics for response variables investigated.

Source	Sequential <i>p</i> -Value	Lack of Fit <i>p</i> -Value	Std. Dev.	R ²	Adjusted R ²	Predicted R ²	Remarks
Sb(III) Removal							
Linear	<0.0001	0.0001	7.57	0.8030	0.7575	0.6685	
2FI	0.9824	<0.0001	8.56	0.8061	0.6898	0.3405	
Quadratic	0.0246	0.0002	5.44	0.9452	0.8748	0.1324	Suggested
Cubic	0.0002		0.74	0.9994	0.9976		Aliased
Sb(V) Removal							
Linear	0.9174	<0.0001	44.69	0.0369	−0.1854	−0.7355	
2FI	0.9991	<0.0001	50.90	0.0390	−0.5376	−2.7713	
Quadratic	<0.0001	<0.0001	8.31	0.9821	0.9590	0.7144	Suggested
Cubic	<0.0001		0.70	0.9999	0.9997		Aliased

The predicted response variables (Sb(III)/Sb(V) removal) for BBD were determined by response functions with obtained coefficients (Table 4). The predicted responses presented good correlation with experimental values, as indicated by their regression coefficients (Sb(III)-R²: 0.9452) and (Sb(V)-R²: 0.9821). Table 6 presents the results of the analysis of variance for the two quadratic models as well as regression coefficient R² and adjusted R². It was evident that the modeled responses fitted experimental values well. Hence, the equations were highly reliable. Furthermore, the values of adjusted R² (Sb(III): 0.8748; and Sb(V): 0.9590) suggested that 12% and 4% of the total variation in Sb(III) and Sb(V) removal, respectively, could not be explained by the model. The value of the adequate precision measures the signal to noise ratio (desirable > 4). In the current study, these ratios for Sb(III) and Sb(V) were found to be 12.899 and 15.235, respectively, indicating an adequate signal. Therefore, the chosen quadratic model can be used to navigate the design space (i.e., to predict antimony removal responses) by the C/F/S process.

Table 6. ANOVA results for two second order responses (Sb(III) and Sb(V) removal) modelled.

Source	Sum of Squares	df	Mean Square	F Value	<i>p</i> -Values Prob > F
Sb(III) Removal					
Model	3571.03	9	396.78	13.43	0.0012 *
A-Sb(III) conc	226.24	1	226.24	7.66	0.0278 *
B-FC dose	2461.91	1	2461.91	83.31	<0.0001 *
C-pH	345.36	1	345.36	11.69	0.0112 *
AB	0.66	1	0.66	0.022	0.8858
AC	11.15	1	11.15	0.38	0.5585
BC	0.11	1	0.11	3.685 × 10 ^{−3}	0.9533
A ²	21.33	1	21.33	0.72	0.4237
B ²	158.29	1	158.29	5.36	0.0538
C ²	303.18	1	303.18	10.26	0.0150 *
Lack of Fit	204.64	3	68.21	122.91	0.0002 *
Pure Error	2.22	4	0.55		
R ² = 0.9452, R ² _{adj} = 0.8748, adequate precision = 12.899 (>4)					
Sb(V) Removal					
Model	26,475.55	9	2941.73	42.63	<0.0001 *
A-Sb(V) conc	58.92	1	58.92	0.85	0.3862
B-FC dose	776.38	1	776.38	11.25	0.0122 *
C-pH	159.49	1	159.49	2.31	0.1722
AB	54.02	1	54.02	0.78	0.4056
AC	0.95	1	0.95	0.014	0.9099
BC	2.30	1	2.30	0.033	0.8605
A ²	74.11	1	74.11	1.07	0.3345
B ²	39.18	1	39.18	0.57	0.4757
C ²	24,894.88	1	24,894.88	360.75	<0.0001 *
Lack of Fit	481.10	3	160.37	327.59	<0.0001 *
Pure Error	1.96	4	0.49		
R ² = 0.9821, R ² _{adj} = 0.9590, adequate precision = 15.235 (>4)					

* Significant (*p* < 0.05).

In order to explore the influencing factor responsible for Sb(III, V) removal during the C/F/S process, the linear, interactive, and quadratic effects of factors of two responses were investigated. The statistical significance of the response function generated was checked by F-test and ANOVA results for both response surface quadratic models and model terms (Table 6). In both response functions, the model F value and very low probability values (Sb(III): 0.0012; and Sb(V): <0.0001) indicated that these models were statistically significant and model equations could be adequately used to describe Sb(III, V) removal under various operating parameters. The p value is a statistical parameter used to check the significance of each coefficient. Therefore, factors having p values < 0.05 in both response functions indicate that the model and model terms are statistically significant [30].

For the Sb(III) removal response, the statistical analysis showed that the initial Sb(III) concentration, FC dose, and pH were significant linear terms with one significant quadratic term ($\text{pH} \times \text{pH}$), while the remaining quadratic and interactive terms were found to be insignificant (Table 6). The most significant terms were FC dose and ($\text{pH} \times \text{pH}$) for Sb(III) removal. In contrast, only two factors (i.e., one linear (FC dose) term and one quadratic ($\text{pH} \times \text{pH}$) term) were significant in Sb(V) removal response, with ($\text{pH} \times \text{pH}$) as the most significant term influencing Sb(V) removal. Such results were in good agreement with our previous studies [14–16], in which high FC doses were required to enhance Fe precipitation and achieve good Sb removal in various aqueous matrices. Since other linear, interactive, and quadratic terms were insignificant, they were still considered in Equations (2) and (3) because it was a hierarchical model. In general, the analysis showed that the quadratic model chosen to explain the relationship between factors and response was satisfactory. Thus, it can be used for predicting Sb(III, V) removal efficiencies for a wide range of operating conditions during the C/F/S process.

3.2. Effect of Initial Sb(III, V) Concentration, FC Dose and pH on the Modelled Responses

Three-dimensional response surfaces along with contour plots for two quadratic models generated for the removal of Sb(III) and Sb(V) are presented in Figures 1 and 2. ANOVA results indicated that FC dose and ($\text{pH} \times \text{pH}$) were among the most significant factors for both responses (Table 6). Therefore, independent variables such as FC dose and pH were used to illustrate modelled responses with a third factor, initial Sb(III) and Sb(V) concentrations held at each level investigated: 100 $\mu\text{g/L}$, 550 $\mu\text{g/L}$, and 1000 $\mu\text{g/L}$. In each 3D plot, experimental values are presented as a circle for each design point while model responses are shown as a 3D surface.

Variations in Sb(III) removal efficiency with FC doses at different pHs were observed for initial Sb(III) concentrations of 100 $\mu\text{g/L}$, 550 $\mu\text{g/L}$, and 1000 $\mu\text{g/L}$, as presented in Figure 1a–f. The Sb(III) removal efficiency increased with increasing pH. The optimum pH range for Sb(III) removal by FC coagulation was 6.5–8.5. As evidenced from Figure 1, the lowest Sb(III) removal was observed in the acidic pH range at low initial Sb(III) concentration of 100 $\mu\text{g/L}$. Such an observation may be attributable to the fact that amorphous ferric hydroxide precipitates are unstable at acidic pH conditions [31]. Compared with the Sb(III) response variable, Sb(V) removal was significantly affected by highly acidic and highly alkaline pH conditions (Figure 2a–f). The highest Sb(V) removal was achieved at an optimum pH range of 6.5–7.5 and a medium level of initial Sb(V) concentration (550 $\mu\text{g/L}$). These obtained results were consistent with previous observations, showing efficient Sb(III) removal over a broad pH range and a decline in Sb(V) removal under acidic and basic pH conditions [12,15,16]. The effect of pH range on Sb(III, V) removal efficiency is also related to Fe solubility. It has been previously reported that the presence of Sb(V) species has a remarkable impact on ferric hydroxide precipitates formation at acidic and alkaline conditions, thus enhancing the mobility of Sb(V) species in an aqueous environment [15,16].

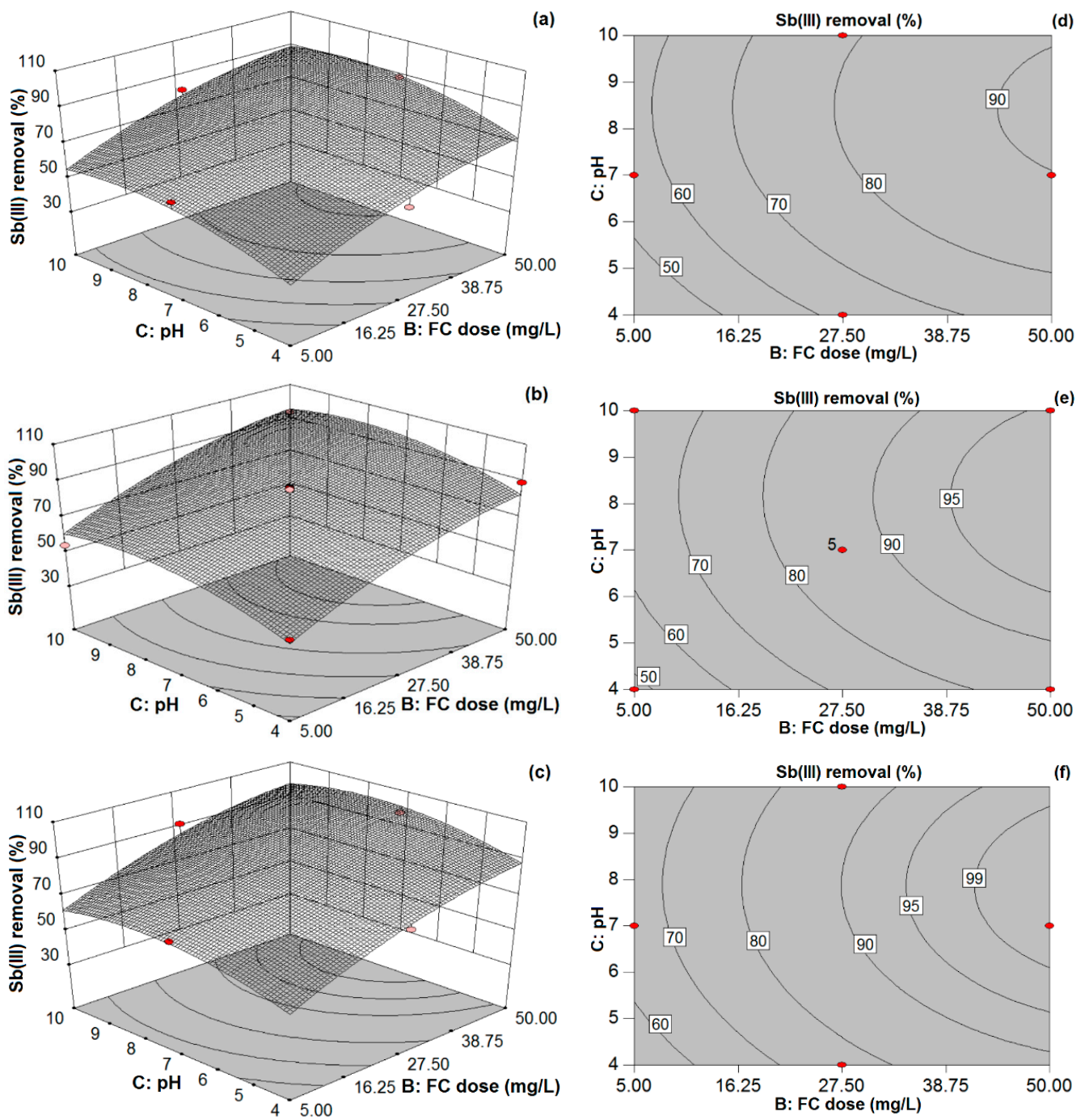


Figure 1. Three-dimensional surface plots and corresponding contour plots showing Sb(III) removal under various pHs (4–10) and FC doses (5–50 mg/L) for an Sb(III) concentration of (a,d) 100 µg/L; (b,e) 550 µg/L; (c,f) 1000 µg/L.

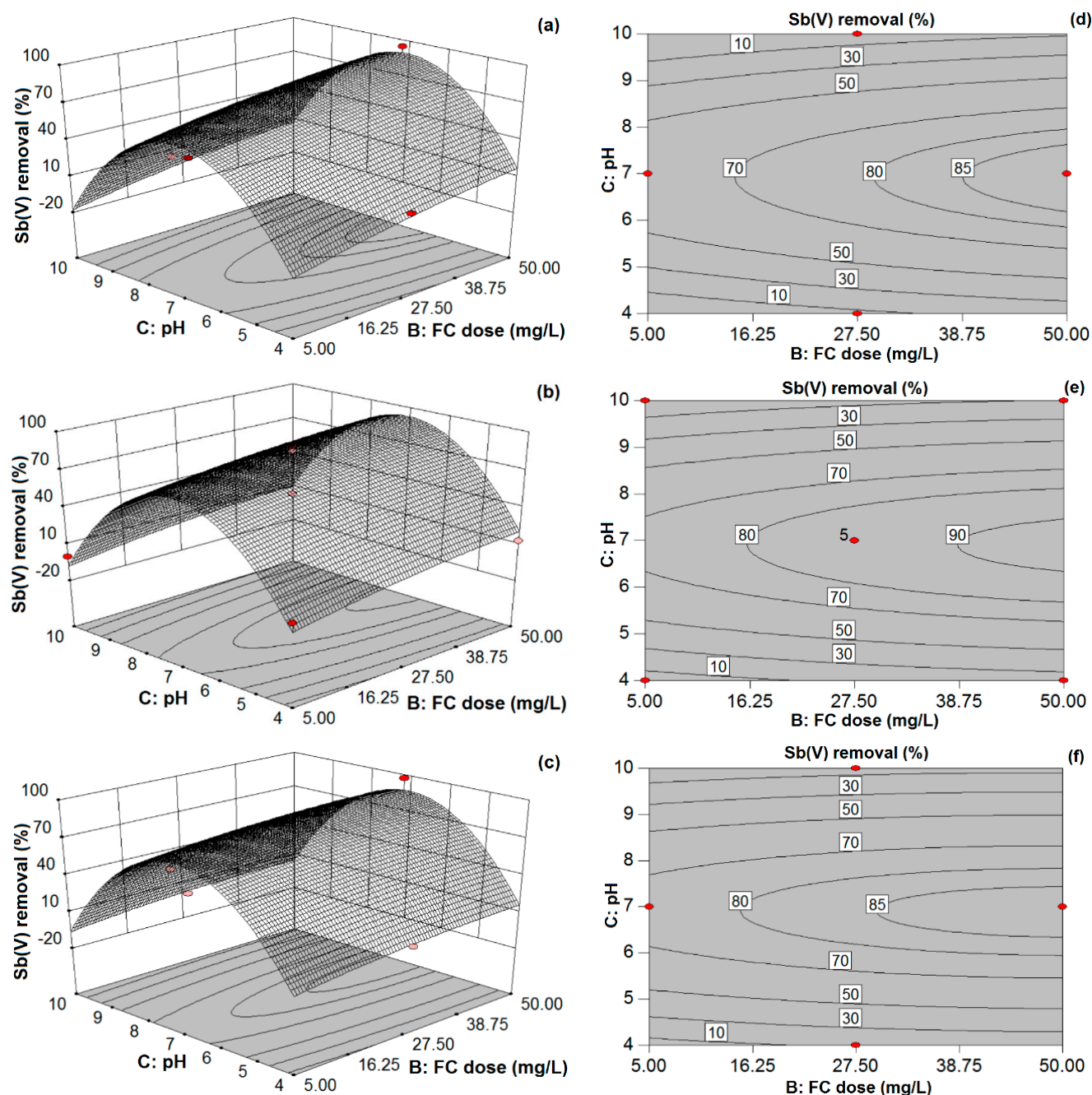
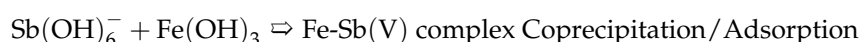
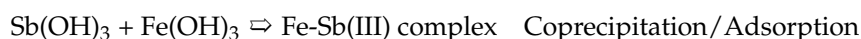
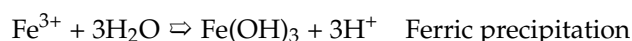
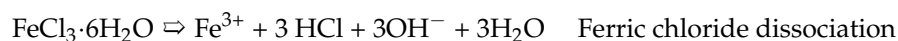


Figure 2. Three-dimensional surface plots and corresponding contour plots showing Sb(V) removal under various pHs (4–10) and FC doses (5–50 mg/L) for an Sb(V) concentration of (a,d) 100 µg/L; (b,e) 550 µg/L; (c,f) 1000 µg/L.

In contrast to the Sb(III) response, the Sb(V) species removal was highly pH dependent, as depicted by the results of BBD for FC. However, the BBD response function did not include the linear effect of pH, but rather incorporated the FC dose followed by the quadratic effect of ($\text{pH} \times \text{pH}$) as the most statistically significant factor for Sb(V) removal. This argument is related to the significant contribution of ($\text{pH} \times \text{pH}$) and FC dose to Sb(V) removal (Table 6). Higher FC doses resulted in improved Sb(V) removal efficiencies across a pH range of 6–8 during the coagulation process, as presented in Figure 2a–f. In general, the dose of ferric chloride is crucial to determine the level of Sb(III, V) removal from water. When FC is added to antimony contaminated water, it dissociates and forms ferric hydroxide precipitates [31]. Precipitation, coprecipitation, and adsorption are three possible mechanisms involved in Sb removal. Since the formation of FeSbO_3 or FeSbO_4

is not favorable under thermodynamic conditions, the precipitation mechanism can be discarded. Initially, coprecipitation (i.e., incorporation of soluble Sb species into a growing iron hydroxide phase via inclusion or exclusion) takes place in an aqueous environment. Furthermore, the uptake of soluble Sb species onto the amorphous iron hydroxide solid surface via adsorption occurs [12,17]. Possible chemical equations of FC coagulation are as follows:



As shown above, an increase in FC dose would cause a substantial increase in Sb(III, V) removal by complexation of Sb species with iron hydroxide precipitates. Therefore, the BBD design also presented FC dose as the most significant factor responsible for Sb(III, V) removal. When the FC dose is increased in aqueous solution, more ferric hydroxide precipitation will occur, resulting in a greater surface area for Sb(III, V) sorption, thereby lowering the residual Sb concentration in contaminated water [32]. However, an increase in Sb(III) removal above a certain FC dose was found to be insignificant in respect of various levels of initial Sb(III) concentrations under optimum pH conditions (Figure 1). For instance, at a low level (100 µg/L Sb(III)), the FC dose of 50 mg/L presented the highest Sb(III) removal at about 91.66%. However, at medium and high levels (550 and 1000 µg/L Sb(III)), the highest Sb(III) removal rates of 97.6% and 98.32% were achieved by FC doses at 45.44 and 40.39 mg/L, respectively. It was noteworthy that a high FC dose was required for a solution with a low initial Sb(III) concentration compared to a higher level of Sb(III) contaminated water. This may be attributable to higher collision probabilities of colloids in Sb(III) rich water as compared to low Sb(III) polluted water [27]. However, an FC dose of 50 mg/L was required to achieve the highest Sb(V) removal rates of 89.46%, 92.71%, and 87.56% for low, medium, and high levels of initial Sb(V) concentration, respectively (Figure 2). These results suggest that the optimization of coagulation parameters plays a significant role in Sb removal from various aquatic environments.

3.3. Model Validation with Independent Experimental Data

Experiments different from the BBD design points and within the range of independent variables were conducted to evaluate the reliability of predicted Sb(III, V) removal responses under optimum coagulation conditions (Table 7). Model predicted values and experimental results were compared to evaluate the validity of the model. Validation experiments confirmed the suitability and accuracy of the model. As the predicted response variables were in close agreement with the experimental results, BBD was a reliable and effective method for determining the optimum coagulation conditions for Sb removal. In general, the current study provided insights into the usefulness and reference conditions for heavy metal removal using BBD for the drinking water industry.

Table 7. Comparison of experimental and predicted Sb(III, V) removal efficiencies under optimum experimental design parameters obtained using Box–Behnken method.

Sb(III, V) Concentration (µg/L)	Sb(III) Species				Sb(V) Species			
	FC Dose (mg/L)	pH	Removal Efficiency (%)		FC Dose (mg/L)	pH	Removal Efficiency (%)	
			Observed	Predicted			Observed	Predicted
100	50	8.43	96	91.66	50	6.91	95	89.46
550	45.44	8.02	95.8	97.60	50	6.90	98	92.71
1000	40.39	7.91	96.4	98.32	50	6.89	97.5	87.56

3.4. Antimony Removal Considering Variations in Residual Iron

The ferric chloride dose has a significant influence on Sb(III, V) removal. However, residual iron (Fe) concentration obtained after the sedimentation/filtration process must be considered owing to its health effects, including gene mutations, skin diseases, and so on. The WHO has recommended the guideline value for Fe in drinking water to be $300 \mu\text{g/L}$ [33,34]. Obtained results in current study indicate that a high FC dose is required to achieve the maximum Sb(III, V) removal efficiency. Therefore, residual Fe concentration was monitored for the solution with a high Sb level to evaluate the C/F/S process. The effect of FC dose on Sb removal and its relationship with residual Fe concentration for a high initial Sb(III, V) concentration level (1 mg/L) are presented in Figure 3. The residual Fe concentration was a function of Sb species type. More residual Fe was observed in the presence of Sb(III) than Sb(V) species. Similar results were observed in our previous study, where Sb(III) species impaired Fe solubility under neutral pH conditions [15]. Above a certain FC dose (40 mg/L), an insignificant increase in Sb(III) removal was observed, where residual Sb(III) concentration slightly decreased but residual Fe increased. Such an observation indicated that an overdose of FC coagulant could result in a high residual level of Fe. Since the maximum allowable concentration of Fe in drinking water is $300 \mu\text{g/L}$, FC is found to be an effective and reliable coagulant due to its residual Fe concentration and high Sb removal affinity from drinking water sources.

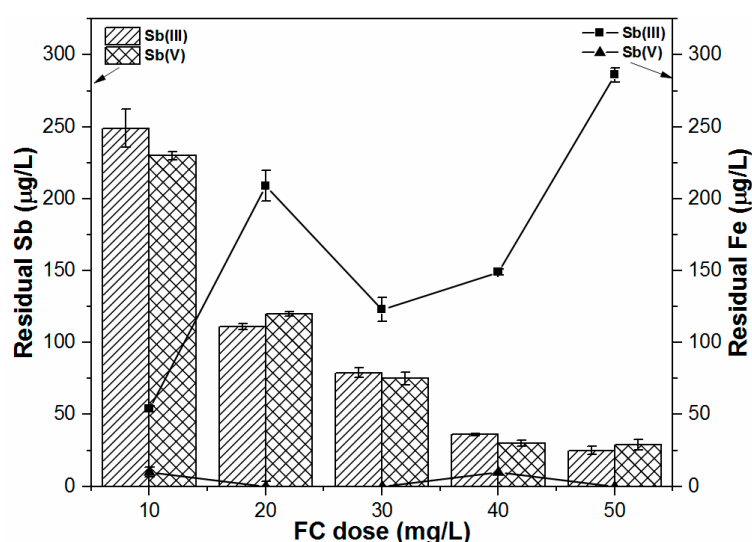


Figure 3. Effect of FC dose (10–50 mg/L) on the residual Fe concentration and Sb(III, V) removal efficiencies under neutral pH (7 ± 0.1), Sb(III, V) concentration (1 mg/L) and temperature ($25 \pm 1^\circ\text{C}$).

3.5. Comparison of Predicted and Actual Antimony Removal Efficiencies in Environmental Water Samples

In order to verify the applicability of the model in aquatic environments, experiments were performed for different synthetic and natural water samples and obtained Sb(III, V) removal results were compared with predicted values, as shown in Figure 4. In order to select desirable operating conditions, two criteria (i.e., minimum and maximum values of FC dose) were obtained from the model. Furthermore, experiments were conducted by selecting minimum and maximum criteria for the FC dose to analyze residual Sb(III, V) concentration in each water sample. The pH of the environmental water sample was readjusted after the addition of a selected amount of FC dose. For all studied waters, the model selected a 50 mg/L FC dose for maximum FC criteria for both Sb(III) and Sb(V) species. However, in the case of minimum FC criteria, the model chose a 5 mg/L FC dose for Sb(V) and an 18.5 mg/L FC dose for Sb(III) species. Such an observation was in good agreement with our previous results (Table 6) showing that the FC dose was the most

significant factor affecting the C/F/S performance of Sb(III) species, as indicated by its p value (<0.0001 for Sb(III) and 0.0122 for Sb(V)).

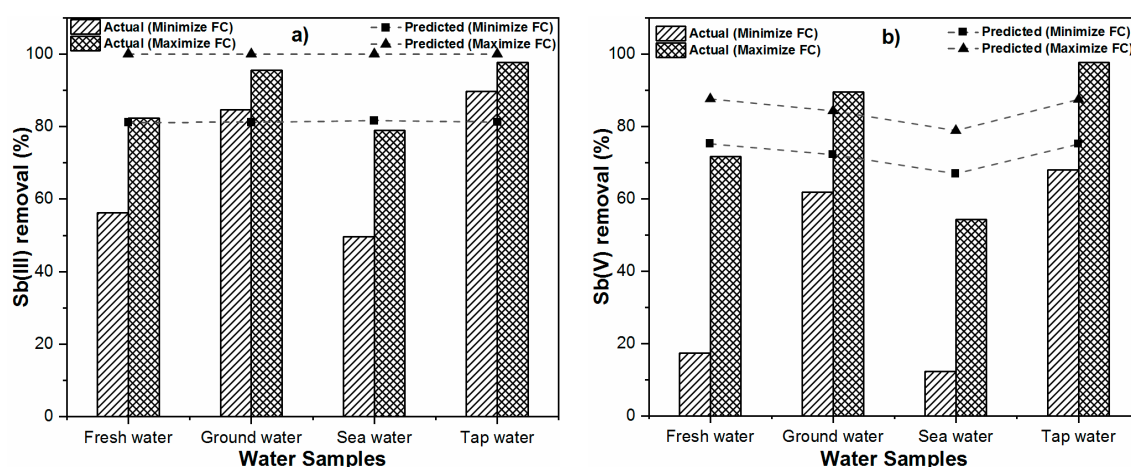


Figure 4. Actual and predicted removal efficiencies of (a) Sb(III) and; (b) Sb(V) for various environmental water samples using the Box–Behnken statistical experiment design (BBD) model with minimizing and maximizing FC dose as a considerable factor.

Sb(III, V) removal efficiencies were evaluated for various water samples (i.e., fresh water, ground water, sea water, and tap water) under relevant environmental conditions (Figure 4). It was noteworthy that a high residual Sb(V) concentration was observed in all water samples as compared to residual Sb(III) irrespective of FC dose. The Sb removal trend obtained after experiments was found to be Tap water > Ground water > Fresh water > Sea water. As shown in Figure 4, an overestimation of Sb(III, V) removal responses in fresh water and sea water and overestimated Sb(V) removal responses in water samples with minimum FC dose criteria were observed. Such a deviation from experimental values might be related to the presence of various competing species in water samples having strong adsorption affinity towards amorphous iron hydroxide precipitates, which might have hindered the complexation of Sb(III, V) species with active Fe surface sites [11,13,14,17]. In contrast, an underestimation of Sb(III) and Sb(V) removal responses was observed for ground water and tap water with minimum and maximum FC dose criteria, respectively. Such an observation might be attributable to the fact that 12% and 4% of the total variations in Sb(III) and Sb(V) removal, respectively, could not be explained by the model (Table 6). Therefore, the presence of other factors might have affected the coagulation behavior of Sb(III, V) species in an integrated environmental system.

To further explore the influencing factors in various aqueous matrices, experimental and predicted values were evaluated based on the characteristics of water samples. It was evidenced that the characteristics of tap water were similar to our model design parameters. Therefore, the experimental results of tap water presented good correlations with the Sb(III, V) removal response variables of our model. For instance, the experimental data for Sb(III) and Sb(V) removal efficiencies in the case of tap water were found to be 89.74% and 67.91%, respectively, close to the predicted responses of 81.22% and 75.11%, respectively, with minimum FC dose criteria. The experimental values of 97.68% and 97.59% were also close to the model values of 100% and 87.46%, respectively. Such a discrepancy in observed values was associated with the presence of bicarbonates (HCO_3^-) known to compete for Fe surface sites with Sb species in tap water [11]. Similarly, ground water also presented a better fitting of experimental data with model values, as presented in Figure 4. A significant decrease in Sb(III, V) removal efficiency was observed for freshwater and sea water samples. High values of total organic carbon (TOC), chlorides, sulfates, and phosphates in these water samples might have resulted in drastic decreases in Sb removal efficiencies (Table 3). It has been demonstrated that organic matter forms stable

complexes onto the Fe surface and, thus, can effectively compete for Fe adsorption sites with Sb species [35]. Similarly, an adverse effect of sulfate on Sb removal has been evidenced in previous studies [36,37], presenting insights into the inner sphere complexation of sulfate with iron oxyhydroxide. The phosphate having identical chemical properties can compete with Sb species in water environments by forming specific inner sphere complexes onto the iron hydroxide surface, thus drastically decreasing the Sb removal efficiency [38]. Furthermore, Fe solubility is remarkably influenced by anionic species in an aquatic environment, thus enhancing the Sb mobility in a heterogeneous system, as evidenced by various studies in the literature [11,14–17]. These findings suggest that the current model may be suitable and appropriate in predicting the optimum coagulation conditions for Sb removal in a natural water environment. Further studies are needed to understand the complex physicochemical interactions between Sb species and various factors in heterogeneous water matrices.

4. Conclusions

In this study, the coprecipitation-adsorption method was employed to determine the effects of various parameters (i.e., Sb(III, V) concentration, FC dose, and pH) on Sb(III, V) removal to achieve statistically reliable results for both pollutants by FC coagulation. BBD and RSM techniques were applied to determine the optimum C/F/S process conditions for maximizing Sb(III, V) removal from water. The obtained results suggest the potential feasibility of the statistical design approach for Sb(III, V) removal and its usefulness for determining the optimal conditions during Sb removal by FC coagulation with limited experimental trials. Experimental results illustrate that FC is an efficient and effective coagulant for Sb(III, V) removal in respect of the required FC dose, residual Fe and Sb(III, V) concentrations. The optimum pH range obtained for Sb(III, V) removal by the C/F/S process was between 6.5 and 7.5. In order to maximize the Sb(III, V) removal performance (88–98%), model responses suggested that the required FC doses were 50 and 40.39 mg/L for low and high initial Sb(III) loading, respectively, while a 50 mg/L FC dose was required for the studied Sb(V) concentration (100–1000 µg/L). Further, the applicability of the model was assessed for different real water samples, in which ground water and tap water spiked with Sb(III, V) solutions showed good agreement for Sb(III, V) removal. However, discrepancies in Sb(III, V) removal were observed for freshwater and sea water samples owing to other influential parameters not incorporated in the current model. Therefore, future research shall focus on complex environmental waters to evaluate the optimum C/F/S conditions for Sb(III, V) removal using statistical modeling.

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Abbreviations

C/F/S	Coagulation-flocculation-sedimentation
BBD	Box-Behnken statistical experiment design
RSM	Response surface methodology
FC	Ferric chloride
USEPA	United States Environmental Protection Agency
EU	European Union
WHO	World Health Organization
ANOVA	Analysis of variance
TOC	Total organic carbon
DI	Deionized
2FI	Two factor interaction model
df	Degree of freedom

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