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Modeling of phosphorus chemical precipitation in aqueous solutions using response surface methodology

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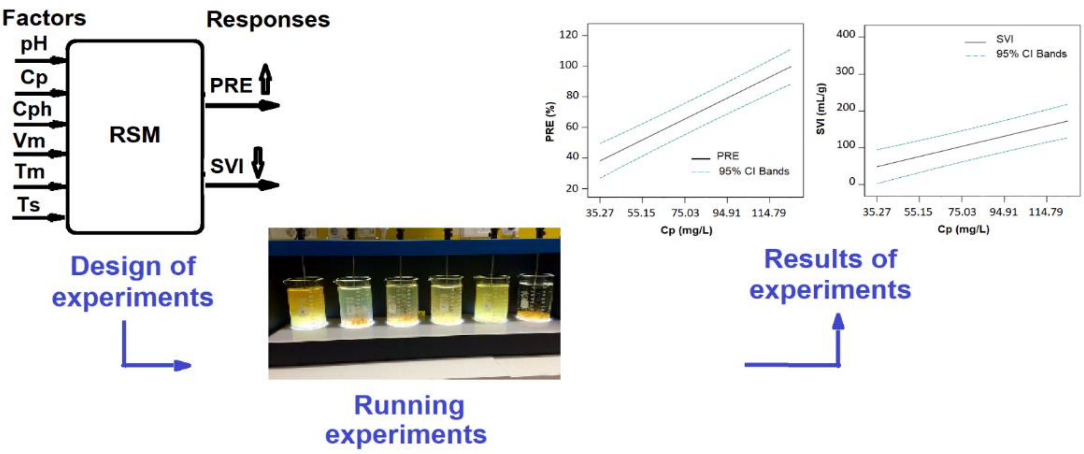
GRAPHICAL ABSTRACT



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ABSTRACT

Phosphorus is one of the main limiting factors for eutrophication in water resources. According to the increasing population and the worsening of the healthy water shortage crisis in recent years, it is necessary to control the concentration of this element (phosphorus) in water resources. This study was performed with the aim of phosphorus removal efficiency (PRE) and sludge volumetric index (SVI) modeling in the chemical precipitation process, and by using poly-aluminum chloride as a precipitator. In this study, the response surface method (RSM) was used based on the central composite design (CCD) to model the effects of pH, the precipitator concentration, mixing time, mixing speed, settling time, and phosphorus initial concentration on the two desired answers including PRE and SVI. Analysis of variances (ANOVA) of the responses showed that among the above factors, precipitator concentration, phosphorus initial concentration, and settling time on phosphorus removal efficiency has been significant. Also, the most important parameters affecting the sludge volume index were precipitator concentration, settling time, and pH. Phosphorus removal efficiency and sludge volume index under optimal condition (pH=7.46, poly-aluminum chloride concentration=104.85 mg/L, mixing time=133 s, mixing speed=152 rpm, settling time=36 min and phosphorus initial concentration= 6.33 mg/L) was predicted to be 84.68% and 151.79 mL/g, respectively. Based on the average responses obtained from three times experiment under predicted optimized conditions, the phosphorus removal efficiency was 80.03%, the sludge volumetric index was 200.07 mL/g. The predicted and obtained data from the experiments showed conformity, which indicates the accuracy of modeling. The findings of this study showed that the factors of precipitator concentration, settling time, and pH should be well controlled to manage the chemical precipitation process using poly-aluminum chloride.

1. Introduction

Increasing population growth, along with the expansion of agricultural and industrial activities to provide food on the one hand and successive droughts in recent years, on the other hand, has led to increased exploitation of freshwater resources in most countries in the arid zone. This process will make countries' water resources more challenging. One of the main solutions to deal with the problem of the water crisis is the optimal use of existing unconventional water and the use of a chain commensurate with the change of its quality in various sectors of consumption (Rouzafzay *et al.,* 2020; Naeemah Bashara and Qaderi, 2024).

Certainly, one of the ways to achieve this is to use agricultural effluents (Janczukowicz and Rodziewicz, 2024). When reusing agricultural effluent in irrigation or discharge to water resource use, one of the points to consider is the pollutants in the effluent. Phosphorus is

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one of the main pollutants in agricultural effluents, which originates from sediments enriched with organic and inorganic phosphate in farm runoff (Ojani *et al.,* 2024).

The entry of phosphate together with nitrate into water sources causes the phenomenon of eutrophication (Irdemez *et al.,* 2006; Pu *et al.,* 2021; An *et al.,* 2024) which in most cases phosphorus is a limiting factor in the occurrence of this phenomenon and not nitrogen because nitrogen fixation occurs naturally by diazotrophs. Thus, most recent studies on nutrient removal have focused on phosphorus removal (Petzoldt, Lezcano and Moreda, 2020; Wang *et al.,* 2021; Liu *et al.,* 2021; Abdolalian and Qaderi, 2022; Fattah *et al.,* 2022; Xu *et al.,* 2024; Zhang *et al.,* 2024; Chen, 2025; Cabo *et al.,* 2025).

Phosphorus in wastewater is observed in various forms such as inorganic phosphorus (orthophosphates and polyphosphates) and organic phosphorus (Özacar and Şengil, 2003a; Feng *et al.,* 2023; Abdoli *et al.,* 2024). In general, phosphorus compounds in wastewater are converted to soluble orthophosphates after hydrolysis and biodegradation. In the chemical precipitation process, orthophosphates react with metal cations resulting from the hydrolysis of chemicals and precipitate (Jiang and Graham, 1998; Yago and Mamuad and Choi, 2024), so the predominant form of phosphorus in natural waters and effluents is orthophosphate which indicates the need to study this form of phosphorus in agricultural effluents (Baird, Eaton and Rice, 2017, p. 4-156; Feng *et al.,* 2023).

So far, several studies have been performed with physical, chemical, and biological methods to remove phosphorus from aqueous solutions and wastewater (Golder, Samanta and Ray, 2006; Irdemez *et al.,* 2006; Kim *et al.,* 2010; Dessì *et al.,* 2024; Abdoli *et al.,* 2024; Chen, 2025). Physical methods such as filtration, ultrafiltration, and reverse osmosis are very expensive or inefficient (Özacar and Şengil, 2003b; Drogui *et al.,* 2008). Biological methods are also less used due to the long retention time, the difficulty of controlling the process, the possibility of returning the digested phosphorus to the effluent, and its low efficiency (Zhao *et al.,* 2009; Abdoli *et al.,* 2024; Chen, 2025). Common chemical methods for phosphorus removal include chemical precipitation and ion exchange (Özacar and Şengil, 2003b; An *et al.,* 2014; Dessì *et al.,* 2024; Xu *et al.,* 2024; Yago and Mamuad and Choi, 2024; Cabo *et al.,* 2025).

Although chemical precipitation has disadvantages such as high operating costs, high sludge production, very hard drainage of sludge and pH change problems (Bektas *et al.,* 2004; Zhao *et al.,* 2009; Fattah *et al.,* 2022), but this method is currently the most commonly known process among phosphorus removal methods and is widely used (An *et al.,* 2014; Petzoldt, Lezcano and Moreda, 2020; Dessì *et al.,* 2024; Xu *et al.,* 2024; Yago and Mamuad and Choi, 2024; Cabo *et al.,* 2025). One of the advantages of the chemical precipitation method is that it can be designed and implemented in a short time. Therefore, this method can be used in crises (Mesdaghinia *et al.,* 2003). Accordingly, in the present study, chemical precipitation was chosen to remove phosphorus from aqueous solutions.

One of the main parameters in the design of the chemical precipitation process is the selection of the precipitator. Although in the past, metal salts (iron, aluminum) and lime have been commonly used as precipitators in the chemical precipitation process of phosphorus (Metcalf and Eddy, 2003), in recent years, a new type of mineral polymer coagulant called poly-aluminum chloride has been introduced, which has become popular and used in many parts of the world. Poly-aluminum chloride is one of the most important mineral polymers with the symbol PACl and the general formula $[Al_2(OH)_xCl_{(6-x)} \cdot YH_2O]$, which is more widely used than other species (Wang *et al.,* 2004; Shi *et al.,* 2007; Murnane *et al.,* 2015; Sha *et al.,* 2021; Sha *et al.,* 2022; Li, Duan and Li, 2022; Wang and Duan, 2024). A wide pH range, easier application due to faster and better dissolution, less residue than other metal compounds, high efficiency in phosphorus removal, reduction of sludge production, and ease of dewatering are among the advantages of poly-aluminum chloride, which increase its use in water treatment (Grover, 1989; Kan and Huang, 1998; Aguilar *et al.,* 2005; Zouboulis and Tzoupanos, 2009, Zouboulis and Tzoupanos, 2010; Murnane *et al.,* 2015; Sha *et al.,* 2021; Li, Duan and Li, 2022; Duan *et al.,* 2022; Sha *et al.,* 2022; Wang and Duan, 2024). Due to the above reasons, in this study, poly-aluminum chloride was used as the precipitator in the chemical precipitation process.

In fact, in this study, the chemical precipitation of phosphorus from aqueous solutions using poly-aluminum chloride has been modeled. The aim of this modeling is to achieve the highest phosphorus removal and the lowest volume of sludge. Modeling in this study was performed using the response surface methodology (RSM). This method is a powerful statistical and mathematical tool used to model and optimize complex processes in which multiple input variables affect an output response. This method is particularly effective in reducing the number of experimental trials required while identifying the optimal conditions for a desired response. Originally developed for the optimization of industrial and chemical processes, this method has found wide applications in various fields, including environmental engineering, pharmaceuticals, food technology, agriculture, and materials science. The ability of this method to efficiently investigate interactions between variables makes it a valuable tool for process improvement and innovation (Zoqi, Ayobi and Khataei, 2023; Yaseri, Qaderi and Khataei, 2024; Khataei, Qaderi and Mosavat, 2025).

2. Materials and methods

2.1. Preparation of phosphorous solution

In this study, a solution with a concentration of 100 mg/L of phosphorus was made to supply phosphate-contaminated aqueous solutions (artificial wastewater) using tap water and triple superphosphate fertilizer. This solution was then used as the stock solution to adjust the initial concentration of phosphorus in each sample.

2.2. Method of phosphorus chemical precipitation process

A jar test apparatus was used to perform the chemical precipitation process. In these experiments, the parameters of solution pH, chemical concentration, time and speed of mixing, and settling time were adjusted according to the conditions determined by the experiment design software. The initial concentration of phosphorus was adjusted in samples with a volume of 1000 mL and then the pH of the samples was adjusted. Normal solutions of hydrochloric acid and sodium hydroxide were used to adjust the pH of the samples in each experiment depending on the pH selected for each sample. After adjusting the initial concentration and pH, poly-aluminum chloride powder was added to each sample based on the amount specified in the experiment design software. The specimens were then shaken at a specified time and speed according to the conditions specified in the experiment design. The samples were kept still for a certain period of time for settling at the end of each experiment. After the settling step, a volume of the supernatant liquid of the sample was taken in a glass container using a pipette to measure the concentration of residual phosphorus in the sample.

2.3. Phosphorus analysis method

In this study, the ascorbic acid method with No. 4500-PE presented in the book entitled Standard Methods for the Examination of Water and Wastewater has been used to measure the concentration of soluble phosphorus (orthophosphate) in each sample (Baird, Eaton and Rice, 2017, p. 4-164).

2.4. Measuring the PRE

After measuring the solution phosphorus of the sample before and after the chemical precipitation process of each experiment, Eq. 1 was used to calculate the removal efficiency of dissolved phosphorus.

$$\text{P removal \%} = \frac{\mathrm{P_{(in)}} - \mathrm{P_{(out)}}}{\mathrm{P_{(in)}}} \times 100\% \qquad (1)$$

where, P_{in} and P_{out} are the initial and final concentrations of soluble phosphorus in the sample under chemical precipitation, respectively.

2.5. Measurement of SVI

To measure the SVI, the 2710-D method presented in the book entitled Standard Methods for the Examination of Water and Wastewater has been used (Baird, Eaton and Rice, 2017, p. 2-94).

2.6. Design of experiment

The RSM consists of computational methods based on the experimental data and is used in previous researches (Qaderi, Sayahzadeh and Azizi, 2018; Qaderi *et al.,* 2019; Khourshidi and Qaderi, 2023; Ahmadi *et al.,* 2023). According to much previous researches, Design-Expert 11 software and the RSM with the CCD were used to determine the number of experiments in this research, to evaluate the effect of each factor on the performance of the chemical precipitation process, and also to optimize the values of those factors. To design the experiments of this study, first the factors affecting the process of phosphorus chemical precipitation were identified and selected based on the research literature. Factors influencing the chemical precipitation process of phosphorus were pH, precipitator concentration, mixing time, mixing speed, settling time, and initial phosphorus concentration, which were selected as the main factors for optimization. The two studied responses are included PRE and SVI. The effect of all factors and their interactions on the responses were studied by performing experiments at 5 different levels (α +, 1 +, 0,1-, α-). The range and values defined for these six variables were determined based on previous studies in this field and the results of preliminary experiments. The different levels of independent variables are presented in Table 1.

Table 1. The range and defined levels of factors in the CCD.

Factors	Sign	Range	Code and levels of factors				
			-α	-1	0	+1	+α
pH of solution	pH	5-8	5	5.541	6.499	7.458	8
The concentration of precipitator (mg/L)	Cp	10-150	10	35.274	80.001	124.728	150
The initial concentration of phosphorous (mg/L)	Cph	5-10	5	5.902	7.499	9.097	10
The mixing speed (rpm)	Vm	30-180	30	57.079	105	152.921	180
The mixing time (sec)	Tm	30-600	30	132.901	312	497.099	600
The settling time (min)	Ts	30-60	30	35.415	44.999	54.584	60

The number of experiments was calculated using Eq. 2 where N is the number of experiments, k is the number of independent variables (factors) and C_0 is the number of center points (Khalegh and Qaderi, 2019); Therefore, in this study, a CCD was performed with 64 factorial points, 12 axial or star points and 10 replications at the center point and a total of 86 experiments. The experiments results are presented in Table 2.

$$N=2^K+2K+C_0 \tag{2}$$

2.7. Method of analyzing experiments results

By performing the statistical test of ANOVA, while identifying the factors affecting the response value, ineffective factors and items were removed from the selected model. The significance or non-significance of each of the model coefficients provided by the software was evaluated by examining the p-values. The quality of the appropriate models was evaluated by examining the coefficient of determination (R^2) and the adaptive coefficient of determination (Adjusted R^2).

After modifying the model, two-dimensional charts of regression models were used to visually and graphically examine how each of the factors affecting the response value. Also, based on the modified model and whether the maximum or minimum amount of response is desirable for the research, the software determined the maximum or minimum points of the response surface as the optimal response points and the values of the effective factors at these points as the optimal response conditions. Finally, the response values obtained from the experiments under the declared optimal conditions were compared with the response values predicted by the software to validate the model prediction for the optimal response.

3. Results and discussion

3.1. Results of designed experiments

The results of three replications of 86 experiments designed based on the RSM with a CCD have been obtained according to Table 2. These results including the removal efficiency of soluble phosphorus and the volume index of precipitated sludge.

3.2. PRE analysis

3.2.1. Model selection and ANOVA

To analyze the data related to PRE, among the Mean, Linear, 2FI, Quadratic, and Qubic models, the Quadratic model was selected because it had the highest correlation with the data related to PRE. The significance of the selected model and the defined items depends on the amount of p-value. The presence of p-values less than the significance threshold ($p<0.05$) for the regression model and p-values more than the significance threshold ($p>0.05$) for lack of fit indicates the significance and efficiency of the model. Based on the results of ANOVA of PRE data, the p-value for the regression model and lack of fit were estimated to be less than 0.0001 and 0.5605, respectively, which indicates the significance and efficiency of the selected model.

3.2.2. The main effects of the factors

According to the ANOVA of PRE data, among all the items of the model, only the main effects of the factors of precipitator concentration (B), settling time (E) and initial phosphorus concentration (F), and components BD, BE, BF, DE, EF, A^2, D^2 have p-values less than 0.05 and therefore their effect on PRE is significant.

Additionally, the factor that has the most significant effect on the PRE has the lowest p-value. Therefore, according to the ANOVA of the PRE data, the highest main effects of the factors on the chemical precipitation of soluble phosphorus were related to the precipitator concentration (B), the initial phosphorus concentration (F), and the settling time (E), respectively. Fig. 1 shows how these three factors affect the PRE.

It is observed that the precipitator concentration and settling time have a direct effect on PRE, i.e. with increasing the precipitator concentration and settling time (in the study range), the PRE will increase. However, the initial phosphorus concentration has the reverse effect on the PRE. This means that as the initial phosphorus concentration increases, the PRE will decrease.

Another important point is that no significant effect was observed for the pH factor, while in several studies, pH has been reported as an effective factor in PRE (Zouboulis and Tzoupanos, 2009; Caravelli, De Gregorio and Zaritzky, 2012; An *et al.,* 2014). The reason for this is the selection of a very limited range of 5 to 8 for pH factor in the designed experiments. Therefore, the range defined for each factor can play a major role in whether or not that factor is effective on response value changes

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3.2.3. The interaction effects of the factors

Fig. 2 shows the interaction of the factors on the PRE. The presence of cross lines means that a decrease or increase in the amount of one effective factor will change the effect of another factor on the response.

Table 2. Conditions and results (answers) of 86 designed experiments.

Runs	Factors						Responses		Runs	Factors						Responses	
	pH	Cp (mg/L)	Tm (s)	Vm (rpm)	Ts (min)	Cph (mg/L)	PRE (%)	SVI (mL/g)		pH	Cp (mg/L)	Tm (s)	Vm (rpm)	Ts (min)	Cph (mg/L)	PRE (%)	SVI (mL/g)
1	7.46	35.27	132.90	153	35	5.90	17.50	68.18	44	7.46	124.73	132.90	153	55	9.10	91.19	198.28
2	6.50	80.00	315.00	105	45	9.10	23.64	100.00	45	7.46	35.27	132.90	57	55	9.10	41.02	76.09
3	6.50	80.00	30.00	105	45	9.10	27.27	166.67	46	6.50	80.00	315.00	180	45	7.50	91.09	180.56
4	7.46	124.73	497.10	57	35	5.90	41.08	166.67	47	5.54	35.27	132.90	153	55	7.50	38.38	125.00
5	6.50	80.00	315.00	105	45	7.50	32.47	208.33	48	6.50	80.00	315.00	105	45	5.90	95.33	295.45
6	6.50	80.00	315.00	105	45	5.90	23.75	171.05	49	6.50	80.00	315.00	105	45	7.50	86.49	270.83
7	5.54	124.73	132.90	153	35	9.10	47.79	169.35	50	5.54	124.73	497.10	153	35	7.50	96.04	266.67
8	5.54	124.73	132.90	57	35	5.90	73.07	178.57	51	7.46	35.27	132.90	57	55	9.10	39.33	68.18
9	5.54	124.73	497.10	153	35	7.50	40.60	316.67	52	7.46	124.73	497.10	57	55	5.90	90.02	345.24
10	6.50	80.00	315.00	105	60	5.90	26.42	283.33	53	5.54	124.73	132.90	57	55	5.90	93.12	339.29
11	5.54	35.27	132.90	57	35	9.10	4.00	78.13	54	7.46	35.27	132.90	57	35	9.10	27.84	194.44
12	7.46	124.73	132.90	57	35	9.10	56.02	108.70	55	5.54	124.73	497.10	153	55	5.90	97.24	250.00
13	5.54	124.73	497.10	57	35	5.90	85.40	321.43	56	7.46	35.27	497.10	57	35	5.90	26.68	107.14

14	5.54	124.73	132.90	153	55	9.10	53.39	308.82	57	7.46	124.73	132.90	153	35	9.10	95.52	238.10
15	5.54	35.27	497.10	153	35	7.50	53.22	166.67	58	5.54	124.73	132.90	57	55	5.90	65.43	179.69
16	6.50	80.00	315.00	105	45	5.90	25.79	129.63	59	5.54	124.73	497.10	57	55	5.90	89.53	250.00
17	5.54	35.27	497.10	57	35	7.50	8.69	34.46	60	5.54	35.27	497.10	153	55	5.90	28.43	125.00
18	6.50	80.00	315.00	105	30	9.10	27.74	.150.0 0	61	7.46	35.27	132.90	153	35	5.90	8.70	138.89
19	6.50	80.00	315.00	105	45	5.90	28.67	222.22	62	6.50	80.00	315.00	105	45	9.10	32.19	321.43
20	6.50	80.00	600.00	105	45	5.90	27.62	375.00	63	5.54	124.73	132.90	153	55	9.10	90.53	403.85
21	7.46	35.27	497.10	153	35	9.10	10.64	34.46	64	7.46	124.73	497.10	153	55	9.10	53.12	300.00
22	7.46	35.27	497.10	57	35	5.90	13.89	117.65	65	7.46	35.27	132.90	153	55	9.10	6.76	138.89
23	6.50	80.00	315.00	105	45	7.50	27.33	132.35	66	7.46	35.27	497.10	57	55	9.10	29.24	250.00
24	5.54	124.73	132.90	153	35	9.10	85.31	128.38	67	5.54	35.27	132.90	153	35	9.10	6.78	38.46
25	7.46	124.73	132.90	57	35	5.00	43.10	179.69	68	5.54	124.73	497.10	57	35	9.10	72.30	294.12
26	5.54	124.73	497.10	57	55	7.50	77.83	53.57	69	6.50	150/00	315.00	105	45	7.50	92.67	388.89
27	5.54	35.27	132.90	57	55	5.90	43.31	166.67	70	5.00	80.00	315.00	105	45	7.50	47.77	541.67
28	6.50	10.00	315.00	105	45	9.10	2.22	10.87	71	7.46	35.27	132.90	153	55	5.90	5.02	78.95
29	7.46	124.73	497.10	153	55	9.10	86.59	150.00	72	6.50	80.00	315.00	105	45	7.50	57.36	121.43
30	5.54	35.27	497.10	153	55	5.90	24.25	166.67	73	6.50	80.00	315.00	105	45	7.50	73.16	181.82
31	5.54	35.27	497.10	57	55	9.10	3.52	187.50	74	7.46	124.73	132.90	153	35	9.10	77.44	189.66
32	6.50	80.00	315.00	105	45	9.10	47.50	104.17	75	5.54	35.27	132.90	153	55	5.90	20.96	52.63
33	7.46	124.73	497.10	57	55	5.90	77.39	114.29	76	7.46	35.27	497.10	153	35	5.90	21.10	34.46
34	5.54	35.27	132.90	57	55	5.90	32.24	69.44	77	7.46	35.27	497.10	153	55	9.10	27.12	27.78
35	7.46	124.73	132.90	57	55	9.10	81.47	175.68	78	7.46	124.73	497.10	57	35	5.90	89.92	222.22
36	5.54	35.27	132.90	153	35	5.90	45.47	350.00	79	5.54	124.73	497.10	153	55	5.90	99.23	226.19
37	5.54	124.73	132.90	57	35	5.90	89.64	174.24	80	5.54	35.27	497.10	57	55	9.10	26.17	69.44
38	8.00	80.00	315.00	105	45	5.90	78.93	266.67	81	5.54	35.27	497.10	57	55	5.90	30.94	125.00
39	7.46	35.27	497.10	57	55	7.50	41.81	194.44	82	7.46	124.73	132.90	57	55	5.90	88.30	269.23
40	6.50	80.00	315.00	30	45	5.90	79.77	152.17	83	7.46	124.73	132.90	153	55	5.90	95.03	166.67
41	5.54	35.27	497.10	153	35	9.10	34.57	69.44	84	7.46	35.27	497.10	153	55	5.90	6.88	22.73
42	7.46	35.27	132.90	57	35	9.10	44.06	86.96	85	5.54	35.27	132.90	57	35	9.10	24.38	10.87
43	7.46	124.73	497.10	153	35	9.10	97.55	142.86	86	7.46	124.73	497.10	153	35	9.10	81.19	172.41

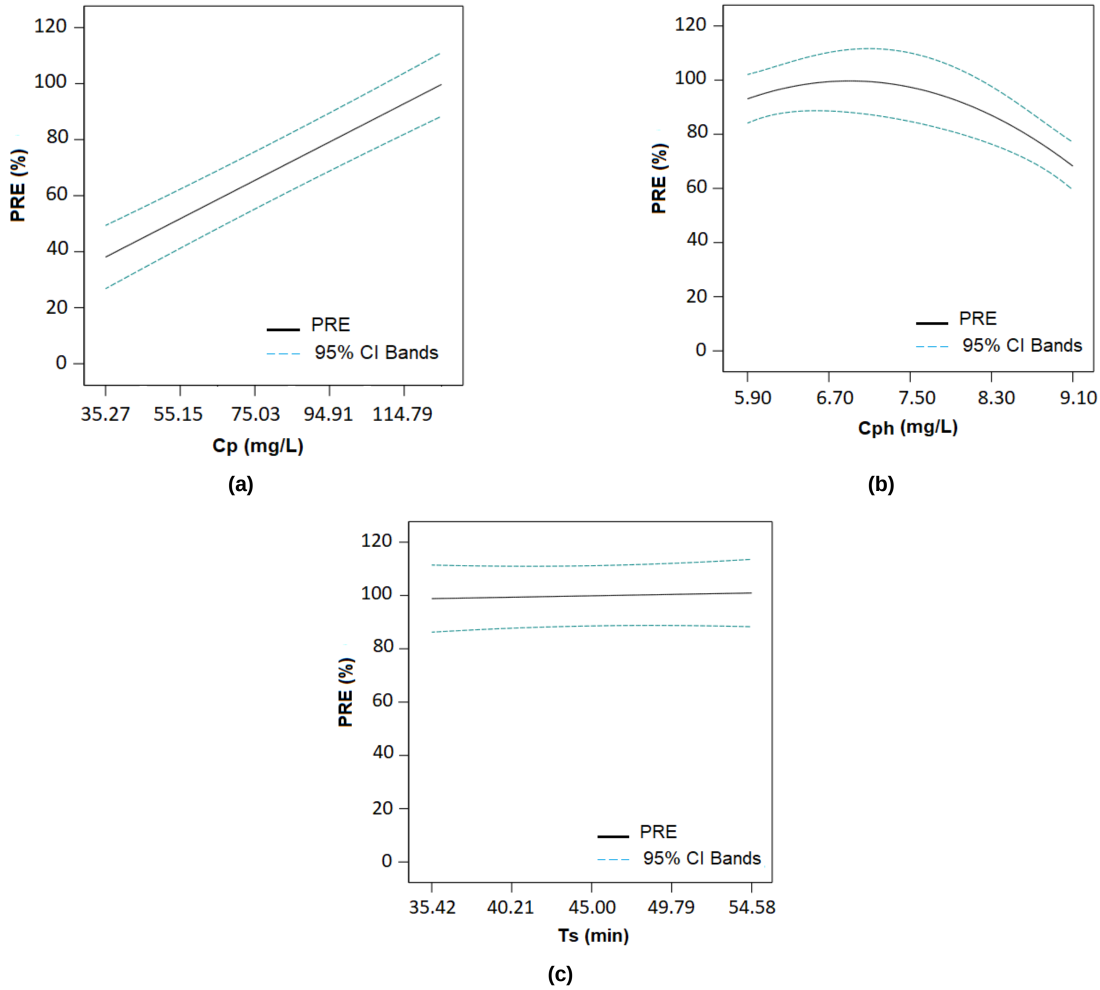

Fig. 1. The main effects of Cp (a), Cph (b) and Ts (c) on the PRE.

Fig. 2a shows that there is a direct interaction between the two factors of precipitator concentration (B) and mixing speed (D) on the PRE. That means, increasing the mixing speed cause to increase in the PRE due to the increase in the precipitator concentration. This synergy is because higher mixing speed causes more dispersion and distribution of precipitator particles in water containing phosphorus soluble ions and therefore increases the contact and reaction between phosphorus soluble ions with precipitator particles. As a result, more ions of soluble phosphorus are precipitated and separated from the water.

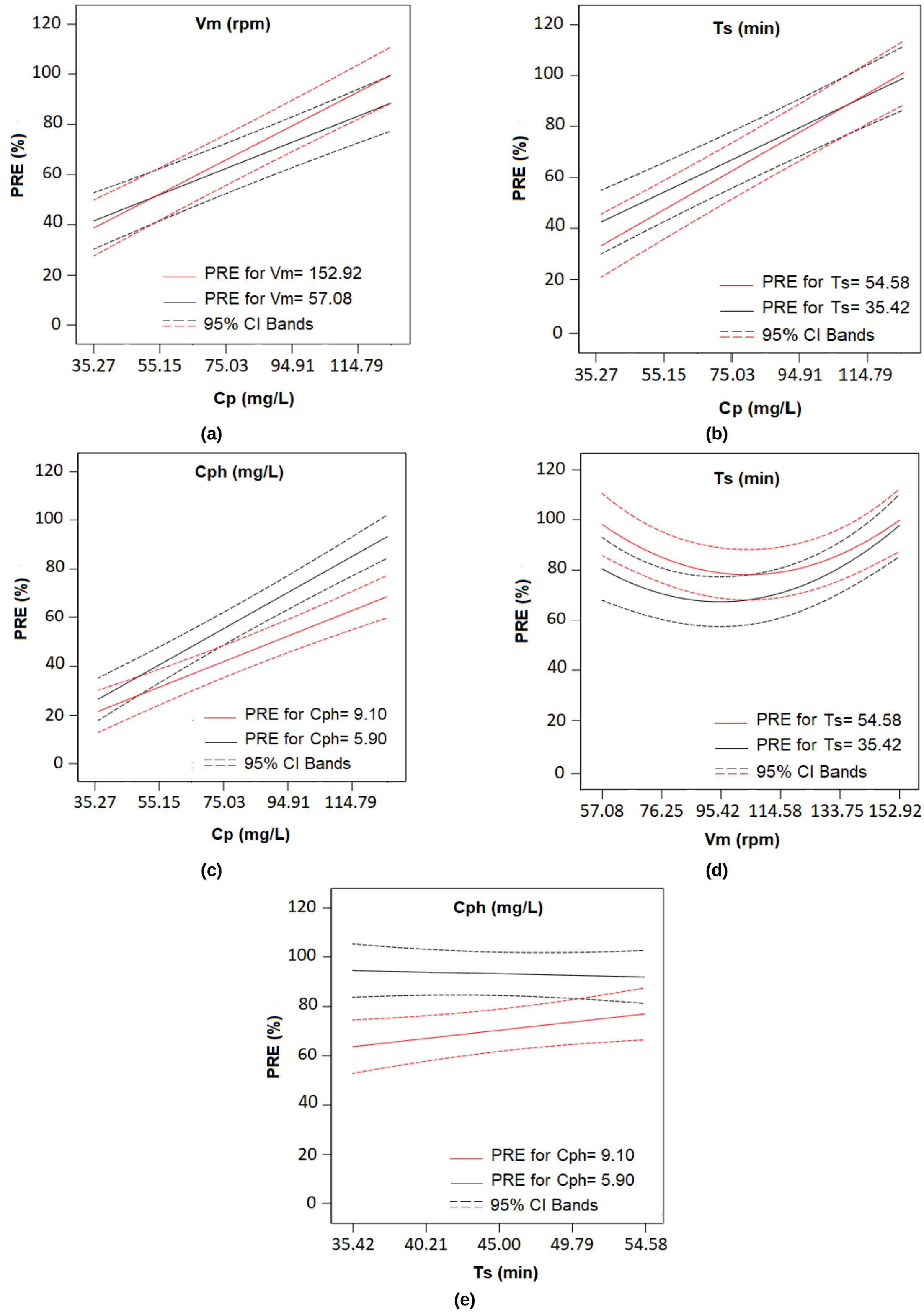

Fig. 2. Interaction effects of factors on the PRE, (a) interaction between Cp and Vm, (b) interaction between Cp and Ts, (c) interaction between Cp and Cph, (d) interaction between Vm and Ts, (e) interaction between Ts and Cph.

Fig. 2b also shows that there is direct interaction between the two factors of precipitator concentration (B) and settling time (E) on the PRE. That means, increasing the settling time has caused a further increase in the PRE due to the increase in the precipitator concentration. This synergy is since increasing the settling time provides more opportunity for orthophosphates to come into contact with the metal cations resulting from the hydrolysis of the precipitator. Therefore, more phosphate hydroxides are formed and as a result, more phosphorus soluble ions are precipitated and separated from the water.

Fig. 2c displays that there is inverse interaction between the two factors of precipitator concentration (B) and the initial concentration of phosphorus (F) on the PRE. Thus, with increasing the initial concentration of phosphorus, the rate of increase of PRE decreased slightly after increasing the concentration of precipitator. This decrease is because the ratio of precipitator ions to the number of available phosphorus ions has decreased and as a result, the formation of phosphate hydroxides and PRE have been somewhat reduced.

Fig. 2d shows that there is inverse interaction between the two factors of mixing speed (D) and settling time (E) on PRE. That means, increasing the settling time has resulted in a very small increase in PRE as the mixing speed increases. This change is due to the fact that with increasing settling time, sufficient opportunity for contact and reaction between phosphorus ions with precipitator particles is provided, thus the effect of faster mixing speed on increasing the reaction between phosphorus soluble ions with precipitator particles reduces. Fig. 2e shows that there is a direct interaction between the two factors of settling time (E) and the initial concentration of phosphorus (F) on the

PRE. Thus, at low phosphorus initial concentrations, increasing the settling time did not have a significant effect on the PRE, because the number of soluble phosphorus ions was so small that the minimum settling time has provided ample opportunity for contact and reaction between them with the particles of the precipitator substance; However, with increasing phosphorus initial concentration, the minimum settling time was no longer sufficient for contact and reaction between phosphorus ions with the precipitator particles. Under these conditions, with increasing settling time, more phosphorus ions with precipitator react and precipitate and as a result increase PRE.

3.2.3. Model algebraic equation (response level equation)

After the model items with a p-value greater than 0.1 were removed from the model, the modified form of the quadratic model was obtained as Eq. 3.

$$\% \text{ PRE} = +33.58 + 0.8444\ A + 25.82\ B + 1.29\ D + 3.79\ E - 6.63\ F + 3.53\ BD + 2.87\ BE - 4.95\ BF - 3.94\ DE + 4.01\ EF + 12.15\ A^2 + 21.16\ D^2 - 16.73\ F^2 \quad (3)$$

Eq. 3 estimates the percentage of PRE based on the coded values of the factors. In Equation 3, the positive sign of the coefficients B (precipitator concentration) and E (settling time) indicates the direct effect of these factors on the PRE. The negative sign of coefficient F (initial concentration of phosphorus) also indicates the inverse effect of this factor on the PRE. By comparing the absolute values of the coefficients of these factors, it will be clear that the highest impact of the factors on the PRE was related to the precipitator concentration (B), the initial concentration of phosphorus (F) and the settling time (E), respectively. Since in field applications, the initial concentration of phosphorus is not under control, it can be concluded that in order to properly manage phosphorus removal, the two factors of precipitator concentration and settling time should be properly controlled.

3.3. SVI analysis

3.3.1. Model selection and ANOVA

For the analysis of data related to SVI, the quadratic model was selected due to having the highest correlation with data related to SVI. Based on the results of ANOVA of SVI data, the p-value for the regression model and lack of fit were estimated to be less than 0.0002 and 0.5258, respectively, which indicates the significance and efficiency of the selected model.

3.3.2. The main effects of the factors

According to the ANOVA of SVI data, among all the items of the model, only the main effects of the factors of pH (A), precipitator concentration (B), settling time (E), and component AF have p-values less than 0.05 and therefore their effect on SVI is significant. Additionally, in the selected quadratic model, the factor that has the greatest impact on the SVI has the lowest p-value. Thus, according to the ANOVA of the SVI data, the highest main effects of the factors on the SVI were related to the precipitator concentration (B), the settling time (E), and pH (A), respectively. Fig. 3 shows how these three factors affect the SVI. It is observed that the precipitator concentration and settling time have a direct effect on SVI, i.e. with increasing the precipitator concentration and settling time (in the study range), the SVI will increase. However, the pH has the reverse effect on the SVI. This means that as the pH increases, the SVI will decrease.

3.3.3. The interaction effects of the factors

The effect of the interaction of the factors on the SVI is shown in Fig. 4. Fig. 4a shows that there is inverse interaction between the two factors of mixing speed (D) and pH (A) on SVI. That is, increasing the mixing speed has caused the SVI to decrease more sharply with increasing pH. This behavior can be explained by the fact that by increasing the mixing speed, the contact and reaction between the phosphorus ions with the precipitator particles increases logically, and therefore the amount of sludge increases. Under these conditions, increasing the pH of the solution from the acidic range to the neutral range leads to more neutralization of charged sludge particles and thus reduces the SVI

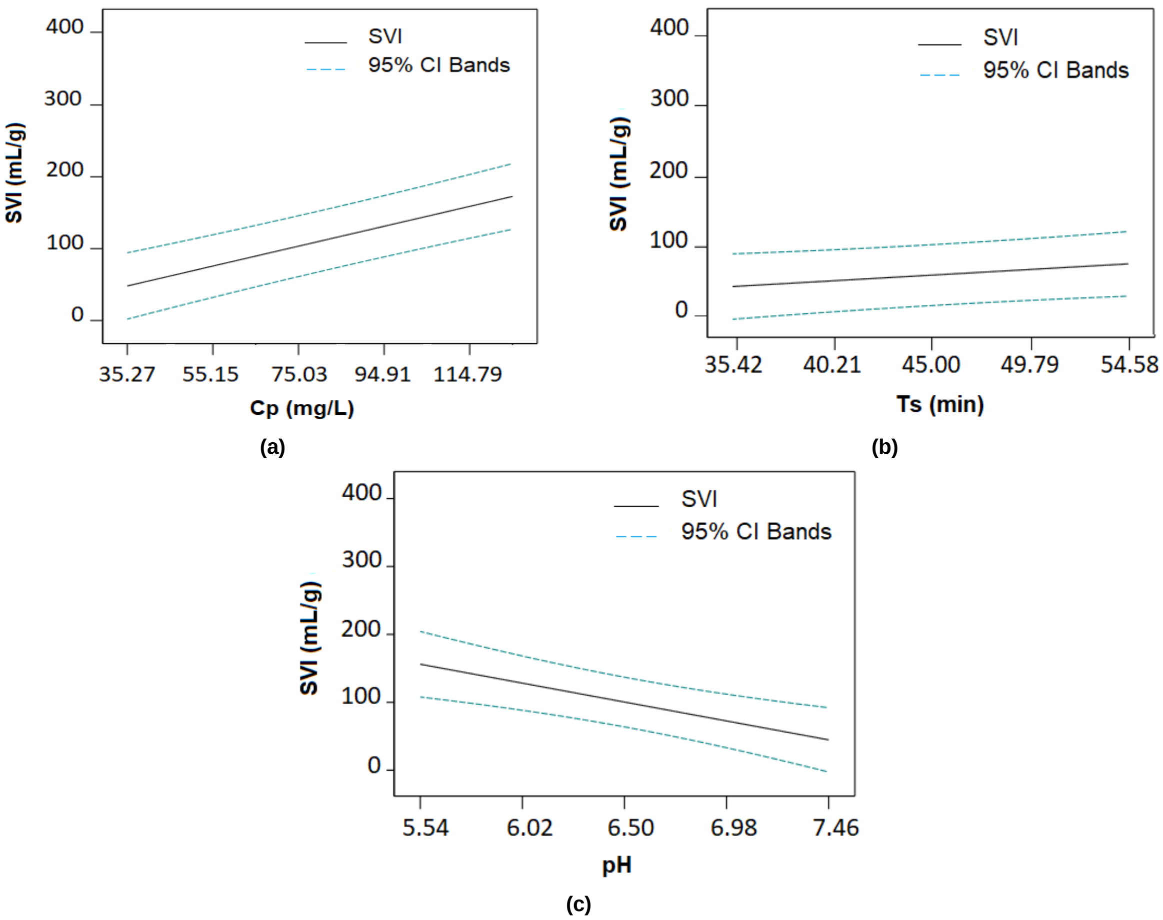

Fig. 3. The main effects of (a) Cp, (b) Ts, and (c) pH on the SVI.

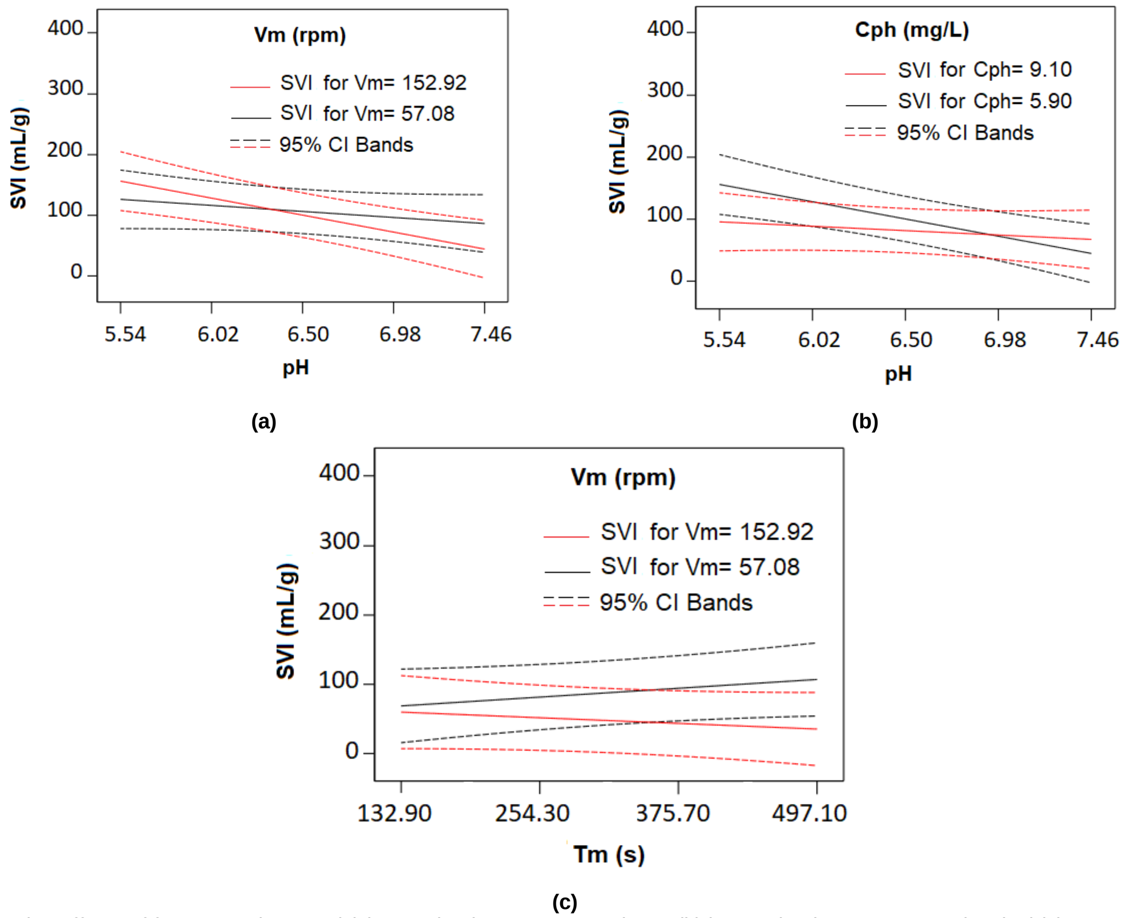

Fig. 4. Interaction effects of factors on the SVI, (a) interaction between pH and Vm, (b) interaction between pH and Cph, (c) interaction between Tm and Vm.

Fig. 4b shows that there is an increasing interaction between the two factors pH (A) and the initial concentration of phosphorus (F) on the SVI in the minimum initial concentration of phosphorus. This means that increasing the phosphorus initial concentration has led to less reduction of the SVI by increasing the pH. That is, increasing the phosphorus initial concentration, has caused the sludge volume index to decrease less with increasing pH. This behavior can also be explained by increasing the phosphorus initial concentration, charged sludge particles have increased somewhat that with increasing the pH from the acidic range to the neutral range, the neutralization of charged sludge particles is reduced and thus the SVI with a smoother slope is reduced. Fig. 4c shows that there is inverse interaction between the two factors of mixing time (C) and mixing speed (D) on SVI. That means, increasing the mixing speed has caused that the SVI decrease with becoming the mixing time longer. This behavior can be justified by the fact that with increasing mixing speed, contact and reaction between phosphorus ions with precipitator particles increased and as a result, the volume of sludge increased. Under these conditions, with increasing mixing time, there is more opportunity for more sludge density and as a result, the SVI decreases.

3.3.4. Model algebraic equation (response level equation)

After the model items with a p-value greater than 0.1 were removed from the model, the modified form of the quadratic model was obtained as Eq. 4.

$$SVI = +167.62 - 17.20\,A + 62.29\,B + 3.45\,C - 3.20\,D + 16.61\,E - 9.42\,F - 18.06\,AD + 20.74\,AF - 15.68\,CD \quad (4)$$

Eq. 4 estimates the percentage of SVI based on the coded values of the factors. In Equation 4, the positive sign of the coefficients B (precipitator concentration) and E (settling time) indicates the direct effect of these factors on the SVI. The negative sign of coefficient A (pH) also indicates the inverse effect of this factor on the SVI. By comparing the absolute values of the coefficients of these factors, it will be clear that the highest impact of the factors on the SVI was related to the precipitator concentration (B), the pH (A), and the settling time (E), respectively. Thus, for proper management of SVI in field applications, the three factors of precipitator concentration, pH and settling time should be properly controlled.

3.4. Optimization of process

To achieve the highest PRE and the lowest SVI, the software suggested that the factors be adjusted with the following values: pH = 7.46, Cp = 104.85 (mg/L), Tm = 133 (s), Vm = 152 (rpm), Ts= 35.81(min) and Cph = 6.33 (mg/L). PRE and SVI under these conditions were predicted 84.68% and 151.79 mL/g by software, respectively. To validate the model prediction, the response value under the optimal conditions predicted by the software was tested experimentally with three replications. Experimental results showed the PRE and SVI under the predicted optimal conditions are 80.03% and 200.07 mL/g respectively. Comparing the results obtained from the experiment with the results predicted by the model, it can be seen that there is not much difference between the laboratory results and the predicted data. Also, the placement of the experiment result (average of three repetitions) in the confidence interval (CI low - CI high), which is calculated by the software at the 95% confidence level (according to Table 3), shows the accuracy and the validity of the experiments and the optimal conditions predicted.

Table 3. Comparison of predicted values and experimental results for optimization of PRE and SVI.

Response	Target	Predicted	Experimental	%95 CI low	%95 CI high
PRE (%)	Maximum	84.68	80.03	75.04	94.33
SVI (mL/g)	Minimum	151.79	200.07	102.01	201.57

4. Conclusions

Among the evaluated factors, only three factors, precipitator concentration, initial phosphorus concentration, and settling time had shown a significant effect on the chemical precipitation of soluble phosphorus. The priority of influence of each of the mentioned factors was the concentration of precipitator (the highest effect), initial concentration of phosphorus, and settling time, respectively. The two factors of precipitator concentration and settling time had a direct effect on the PRE and the initial concentration of phosphorus had an inverse effect on the PRE. For the sludge volume index, only three factors of precipitator concentration, settling time, and pH, had a significant effect on the response. Priority of effect was the precipitator concentration (the highest effect), settling time and pH, respectively. The two factors of precipitator concentration and settling time had a direct effect and pH had an inverse effect on the response. Since in field applications, the initial concentration of phosphorus is not under control, in order to properly manage the PRE and SVI, the three factors of precipitator concentration, settling time, and pH must be properly controlled. It is worth noting that controlling the factors of precipitator concentration and pH reduces treatment costs and prevents further environmental pollution. Under the optimal conditions proposed by the model, PRE and SVI were predicted to be 84.68% and 151.79 mL/g, respectively. Experimental results showed the amount of these two responses in the predicted optimal conditions were 80.03% and 200.07 mL/g. The proximity of the experiment results with the results predicted by the model and also the placement of the experiment results in the confidence interval calculated by the software at 95% confidence level indicates the accuracy and efficiency of the RSM and the selected model.

Conflict of Interest

The authors declare that they have no competing interests.

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Author Contribution

Aghdas Afsharirad: Experiments implementation, writing original draft.
Amir Hossein Sayyahzadeh: Research idea extraction, design of experiments, supervision, analysis and interpretation of data, writing - review & editing.
Shahriar Mahdavi: Deployment of laboratory equipment, control and supervision of experiments implementation.

Data Availability Statement

The dataset used and/or analyzed during the present study is available in the text of the paper.

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