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Optimization of Fe(II)/SPC Sludge Conditioning and Dewatering Process Based on Response Surface Methodology: Full-Scale Application

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Abstract: Sludge conditioning is a crucial step in sludge dewatering aimed at minimizing excessive sludge production. The Fenton process, which harnesses oxidative radicals to dismantle extracellular polymeric substances (EPS) and microorganisms, has been unequivocally proven to enhance sludge dewaterability. However, the widespread adoption of the Fenton process is hampered by its high costs and logistical challenges in transportation. In contrast, the Fe(II)-activated sodium percarbonate (Fe(II)/SPC) process has emerged as a promising technology for sludge conditioning due to its remarkable performance and safe operation. However, limited information is available regarding the optimization of Fe(II)/SPC for sludge conditioning and dewatering at full scale. This study conducted the sludge conditioning and dewatering process within a full-scale wastewater treatment plant, utilizing the response surface methodology (RSM) to optimize the Fe(II)/SPC process. Furthermore, this study investigated its impact on sludge structure and compared the economic benefits of the Fe(II)/SPC process with other full-scale conditioning processes. The results of bound water and LDH analysis revealed that the Fe(II)/SPC process not only degraded EPS but also disrupted microbial cells, thereby releasing intracellular water. Based on the RSM results, we successfully established a polynomial prediction model to determine the optimal capillary suction time (CST) and moisture content. The optimal parameters determined through RSM were an initial pH of 3.02, Fe(II) dosage of 0.05 g/g TSS, and SPC dosage of 0.07 g/g TSS. The validation test confirmed the accuracy of the prediction results, with the conditioned sludge exhibiting a CST of 31.6 s and a moisture content of 51.47%. Furthermore, when compared to the PFS and Fenton processes, the Fe(II)/SPC process demonstrated higher economic efficiency and safety, while maintaining good dewatering performance. Overall, the Fe(II)/SPC treatment shows promise as a prospective sludge dewatering and conditioning process.

Keywords: sludge conditioning; sodium percarbonate; advanced oxidation process; sludge dewaterability

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1. Introduction

Excessive sludge generated by the activated sludge process in wastewater treatment poses significant risks to both the ecological environment and human health. Dewatering, as a crucial step in sludge treatment, offers a solution to minimize sludge volume, reduce environmental burdens, and lower transportation and disposal costs [1]. Consequently, sludge dewatering has emerged as a prominent research focus in recent years [2]. However, sludge dewatering is challenging due to the presence of water within the complex gel-like network formed by the interaction between extracellular polymeric substances (EPS) and microorganisms [3].

The Fenton process has demonstrated effectiveness in EPS degradation, thereby enhancing sludge dewatering capacity [4,5]. Nonetheless, practical application of the Fenton process faces limitations due to the high costs associated with Fenton reagents, safety risks during transportation and storage, and the potential for secondary pollution from its byproducts. In comparison, sodium percarbonate (SPC, $Na_2CO_3 \cdot 1.5H_2O_2$) is a solid compound that can be easily transported. In aqueous media, SPC decomposes into sodium carbonate and hydrogen peroxide. Under acidic conditions, ferrous ions catalyze SPC to produce oxidizing radicals such as hydroxyl radicals (·OH), effectively degrading EPS and promoting sludge dewatering without generating any toxic or harmful substances [6]. Hence, the catalytic effect of Fe(II) on sodium percarbonate (Fe(II)/SPC) has been explored as a promising technology for sludge conditioning and dewatering [7,8].

To enhance the dewaterability of sludge through specific treatments, modeling and optimization techniques are widely employed to predict process parameters. Olivier et al. introduced the drainage index as a parameter to predict the potential thickening quality of flocculated sludge through gravity drainage during sludge conditioning [9]. He et al. utilized uniform design (UD) to determine the optimal experimental conditions for sludge dewatering using a composite conditioner [10]. However, most optimization studies are conducted at the laboratory scale and may not be directly applicable to practical applications. Limited information is available regarding the sludge conditioning process at full scale and the optimization of Fe(II)/SPC for sludge dewatering. Therefore, addressing these research gaps is crucial to improve predictions of sludge dewatering responses.

The response surface method (RSM) is a mathematical and statistical technique used to optimize and analyze multivariate systems [11]. It is commonly employed to investigate the influence of multiple independent variables on one or more response variables, leading to the identification of optimal operating conditions or solutions. RSM holds significant potential for optimizing the dosage of sludge dewatering agents. As sludge dewatering is a complex process involving multiple variables (such as type, dosage, and reaction time) and responses (such as dewatering performance, capillary suction time (CST), and sludge cake moisture content), RSM provides a scientific and efficient means of simulating this complexity. For instance, Cao et al. developed a quadratic multiple prediction model using RSM to determine the solids content of filter cake based on the combination of three conditioners for sludge dewatering [12].

This research aims to optimize the dewatering and conditioning process of actual wastewater treatment plants using RSM for the Fe(II)/SPC process. The evaluation indicators chosen are the sludge CST and the moisture content (W_c) of the sludge cake. Based on RSM experiments, a polynomial prediction model for the optimal Fe(II)/SPC process parameters will be established. Furthermore, the impact of Fe(II)/SPC on the structure of sludge flocs will be investigated, and other conditioning processes will be compared to assess their economic benefits.

2. Materials and Methods

2.1. Materials and Reagents

The waste-activated sludge (WAS) samples were collected from a wastewater treatment plant in Shanwei, Guangdong Province, China. The sludge is transported from the secondary sedimentation tank to the dewatering unit, where 0.4–0.7 mg/g TSS polyacrylamide is added for gravity concentration. The properties of the concentrated sludge are shown in Table S1.

Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (AR, >99.0%) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). SPC ($Na_2CO_3 \cdot 1.5H_2O_2$, 13–14% active oxygen) was purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4, 98%) was obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China).

2.2. Experimental Set-Up

2.2.1. Full-Scale Sludge Conditioning and Dewatering Process

The concentrated sludge was conditioned in a 30 m^3 sludge conditioning tank. The sludge's pH was adjusted with dilute sulphuric acid, followed by the addition of ferrous sulfate and stirring for 10 min. After that, SPC was added and stirred for another 10 min. Samples of the raw sludge and conditioned sludge were taken for analysis of pH, CST, EPS content, and lactate dehydrogenase (LDH) activity.

Full-scale sludge dewatering was performed at the local WWTP (Figure S1). The conditioned sludge was pressed by the plate-and-frame filter. The filter cloth has a warp density of 23.6 root/cm and a weft density of 12.3 root/cm. The pressure applied was 2.3 MPa, the pressure time was 40 min, and the working volume was 30 m^3. Samples of the dewatered sludge cake are collected for W_c tests.

2.2.2. Assessment of Sludge Dewaterability

CST is a crucial indicator of sludge dewatering effectiveness. It refers to the amount of time needed for sludge to penetrate a specific distance on the filter paper. Within a limited range, CST has a positive correlation with a particular resistance. CST tests are performed using a CST instrument (Type 304B, Triton Electronics Ltd., Dunmow, UK) and Whatman No. 17 chromatography grade filter paper with an 18 mm diameter funnel.

The drying and weighing process is used to determine the W_c of the sludge cake. Samples of dewatered sludge are dried at 105 °C until they reach a consistent weight, and then they are chilled in a desiccator. Using Equation (1), the W_c of the filtered sludge cake is determined.

$$W_c = \frac{m_1 - m_2}{m_1 - m_0} \times 100\% \quad (1)$$

where m_0, m_1 and m_2 are the mass of the crucible, the dewatered cake sample and crucible, the dried cake sample and crucible, respectively.

Bound water content (W_b) is determined using a differential scanning calorimetry analyzer (TA DSC25, TA Instruments, New Castle, DE, USA) [7]. The free water in the sample freezes when the temperature of the sludge is initially lowered to −60 °C at a rate of 10 °C/min. The temperature is then raised at the same pace to 40 °C. The peak area of the endothermic curve below the baseline, which reflects the heat necessary to thaw the frozen free water, is used to compute the amount of free water. As a result, the W_b is determined by subtracting the amount of free water from the total water content (Equation (2)) [8].

$$W_b = W_t - \Delta H/\Delta H_0 \quad (2)$$

where W_t is total water content of the sludge samples; ΔH and ΔH_0 are the amount of energy absorbed in the sludge sample and the standard melting heat of ice (334.7 J/g), respectively.

2.2.3. EPS Extraction

Different EPS fractions from the sludge samples, including soluble EPS (S-EPS), loosely bound EPS (LB-EPS), and tightly bound EPS (TB-EPS), were extracted using a modified heat extraction method [13,14]. After centrifuging 50 mL of sludge at 6000× g for 5 min, the fluids in the supernatant were classified as S-EPS. After adding 0.05% (w/w) NaCl solution and stirring for 1 min, the pellet in the centrifuge tube was resuspended to the original volume. The immediately centrifuged solution was treated as LB-EPS after being spun at 6000× g for 10 min. With 0.05% (w/w) NaCl, the leftover pellet was once more resuspended to its original volume and heated to 60 °C for 30 min in a thermostatic water bath. Centrifuging the fluids in the supernatant at 6000× g for 15 min produced the supernatant containing TB-EPS.

2.2.4. Lactate Dehydrogenase Release Assay

The LDH release was assessed using the LDH cytotoxicity assay kit (Shanghai Enzyme-linked Biotechnology Co., Ltd., Shanghai, China) according to the provided instructions. After centrifugation at 12,000× g and 4 °C for 10 min, 10 mL of the supernatant from the sludge samples was added to a 96-well plate. Subsequently, 140 mL of the work solution was mixed with the sludge samples. The mixed solution was then incubated in the dark for 30 min, and the absorbance was measured at 450 nm using a Multiskan FC microplate reader (Thermo Fisher Scientific, Waltham, MA, USA) at room temperature.

2.2.5. Analytical Methods

The pH value was determined using a digital pH meter (PHS-25, INESA Instrument, Shanghai, China). The total suspended solids (TSS) were quantified following a standard method [15]. Protein content was analyzed using the Coomassie Brilliant Blue method [16]. Polysaccharide content was quantified using the anthrone method [17,18]. For the analysis of soluble contents in the sludge, the samples were filtered through a 0.45-μm polyvinylidene fluoride membrane (Millipore, Burlington, MA, USA). Each sample was measured in triplicate, and the mean values and standard deviations are reported.

2.3. RSM Model

Response surface designs typically include the Box–Behnken design (BBD) and central composite design (CCD). While both designs can provide accurate simulation results, BBD requires only three levels for each factor, compared to five levels for CCD. This makes BBD experimentally more convenient than CCD for the same number of factors [19]. Therefore, BBD based on RSM was used to determine the optimal conditions for each variable in the Fe(II)/SPC sludge conditioning process. In a previous laboratory-scale study, it was observed that the dewatering performance of sludge could be significantly improved by employing the Fe(II)/SPC system, with an optimal SFe(II) dosage of approximately 0.7 mmol/g-TSS under acidic conditions. Furthermore, it was determined that the molar ratio of Fe(II) to SPC within the range of 1.5 to 2.0 was the most effective for promoting advanced oxidation [7]. The current experiment entailed an investigation of three independent variables: Fe(II) dosage, SPC dosage, and initial pH, each tested at three different levels as detailed in Table 1. Two key responses, CST and W_c, were examined. The specific ranges for each of these factors were established based on the outcomes of preliminary single-factor experiments.

Table 1. Variable design parameters, range and levels.

Factors	Range and Levels		
	−1	**0**	**1**
X_1, Fe(II) dosage (g/g TSS)	0.018	0.036	0.055
X_2, SPC dosage (g/g TSS)	0.036	0.074	0.110
X_3, initial pH of sludge	2	3	4

The experimental design using Design Expert 13 software is summarized in Table 2. All the experiments were performed in triplicate. Design expert 13 was utilized to model and analyze the experimental results and received the regression mode. Three-dimensional response surface plots of the interactive effects of each factor were plotted. Finally, the optimal conditions for each variable in the process were determined by response surface analysis.

Table 2. BBD experimental design.

Trial No.	Uncoded Variables (Codes) X_1 Fe(II) Dosage (g/g TSS)	X_2 SPC Dosage (g/g TSS)	X_3 Initial pH
1	0	0	0
2	0	−1	1
3	−1	0	1
4	1	−1	0
5	1	1	0
6	0	0	0
7	1	0	−1
8	0	1	1
9	−1	0	−1
10	−1	1	0
11	0	−1	−1
12	0	0	0
13	0	0	0
14	0	0	0
15	0	1	−1
16	1	0	1
17	−1	−1	0

3. Results and Discussion

3.1. Optimal Operation Condition for Fe(II)/SPC Sludge Conditioning by RSM Model

A total of 17 groups of experiments were conducted with the factor levels coded as presented in Table 3. Design Expert 13 was used for the experimental results modeling and analysis of variance, which are shown in Tables 3 and 4. Two second-order polynomial equations are presented for the CST and W_c as a function of the considered factors in the following correlations:

$$\begin{aligned} Y_1 = 159.625 - 90.505X_1 + 5.91X_2 - 52.3725X_3 - 14.6X_1X_2 + 3.05X_1X_3 \\ -1.05X_2X_3 + 42.99{X_1}^2 + 3.9225{X_2}^2 + 8.6475{X_3}^2 \end{aligned} \tag{3}$$

$$\begin{aligned} Y_2 = 108.9875 - 24.67X_1 - 5.26X_2 - 25.815X_3 - 4.85X_1X_2 + 2.85X_1X_3 \\ +0.225X_2X_3 + 10.31{X_1}^2 + 2.6775{X_2}^2 + 3.7275{X_3}^2 \end{aligned} \tag{4}$$

where Y_1 is the CST (s), Y_2 is the W_c (%), X_1, X_2 and X_3 are coded variables of Fe(II) dosage, SPC dosage and initial pH, respectively.

Table 3. ANOVA results for the quadratic model for the CST.

(Response 1: CST) Source	Sum of Squares	df	Mean Square	F-Value	*p*-Value
Model	2505.65	9	278.41	15.57	0.0008
X_1-Fe(II) dosage	1207.86	1	1207.86	67.54	<0.0001
X_2-SPC dosage	118.58	1	118.58	6.63	0.0367
X_3-pH	1.71	1	1.71	0.0957	0.7661
X_1 X_2	213.16	1	213.16	11.92	0.0107
X_1 X_3	9.3	1	9.3	0.5201	0.4942
X_2 X_3	4.41	1	4.41	0.2466	0.6347
${X_1}^2$	486.35	1	486.35	27.19	0.0012
${X_2}^2$	64.78	1	64.78	3.62	0.0987
${X_3}^2$	314.86	1	314.86	17.61	0.0041
Residual	125.19	7	17.88		
Lack of Fit	117.54	3	39.18	20.49	0.0069
Pure Error	7.65	4	1.91		
Cor Total	2630.84	16			

Table 4. ANOVA results for the quadratic model for the W_c.

(Response 2: W_c) Source	Sum of Squares	df	Mean Square	F-Value	p-Value
Model	228.92	9	25.44	10.44	0.0027
X_1-Fe(II) dosage	54.08	1	54.08	22.19	0.0022
X_2-SPC dosage	13	1	13	5.34	0.0542
X_3-pH	0.18	1	0.18	0.0739	0.7936
X_1 X_2	23.52	1	23.52	9.65	0.0172
X_1 X_3	8.12	1	8.12	3.33	0.1106
X_2 X_3	0.2025	1	0.2025	0.0831	0.7815
${X_1}^2$	27.97	1	27.97	11.48	0.0116
${X_2}^2$	30.19	1	30.19	12.39	0.0097
${X_3}^2$	58.5	1	58.5	24.01	0.0018
Residual	17.06	7	2.44		
Lack of Fit	12.13	3	4.04	3.28	0.1405
Pure Error	4.93	4	1.23		
Cor Total	245.98	16			

The analysis of variance (ANOVA) results were used to evaluate the adequacy and significance of the regression models. A p-value less than 0.05 indicates its significance at a 95% confidence level [20]. The p-values of CST and W_c are 0.0008 and 0.0027 in the model (Tables 3 and 4), indicating that the regression model is significant. When R^2 is closer to 1, the empirical model can reflect the experimental data better. The regression coefficient R^2 values are 0.9524 and 0.9307 for CST and W_c regression equation, respectively. Thus, the model fits well and can be used to predict the effects of the three influencing factors on the CST and W_c of conditioned sludge.

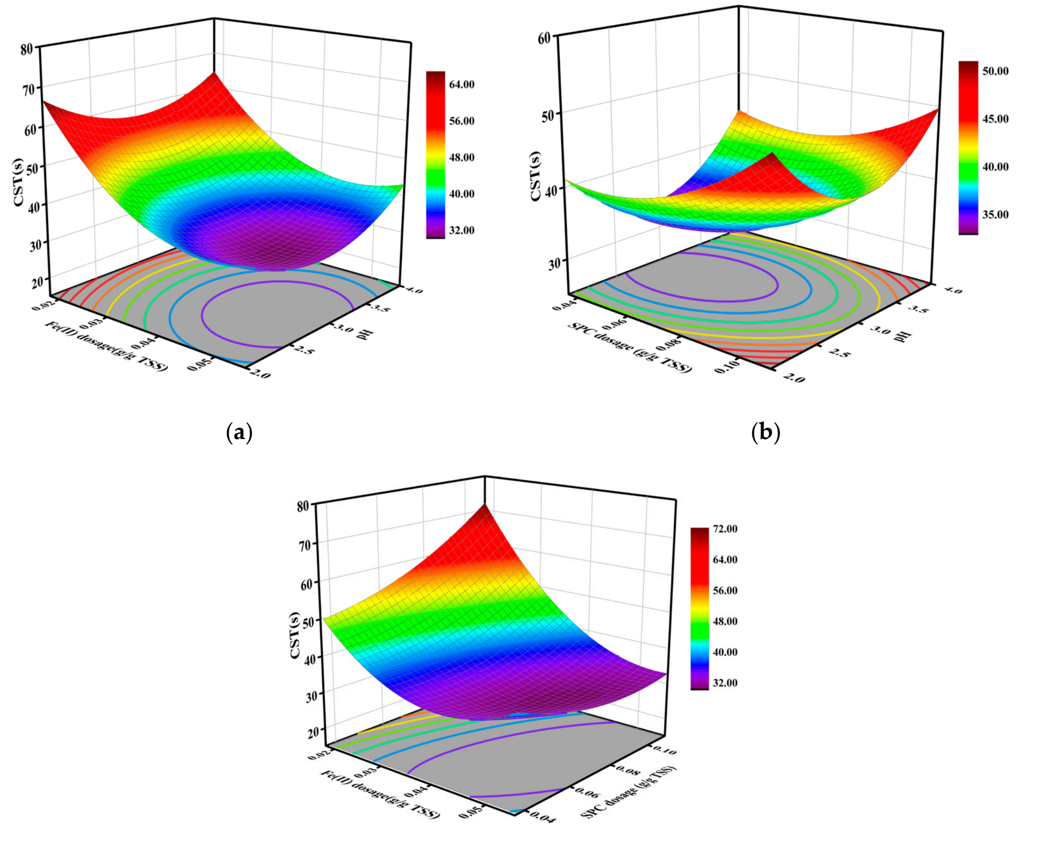
Figure 1 displays the contour plots and 3D response surface plots illustrating the interaction effects of the three factors. The contour line shapes indicate the strength of the interactive effect, with ellipses signifying a significant interaction between two factors and circles indicating the opposite [21]. Analyzing the contours in Figure 1a,b, it can be observed that the interaction between Fe(II) dosage or SPC dosage and initial pH has a less significant effect. In these two graphs, the CST reaches its minimum at an initial pH of 3. Figure 1a demonstrates that the CST gradually decreases with increasing Fe(II) dosage at a low level, likely due to the neutralization of negative charges on the sludge surface by Fe(II) ions, promoting the flocculation of sludge flocs [22]. However, as Fe(II) dosage continues to rise, the CST slightly increases, possibly due to the excessive consumption of ·OH caused by excess Fe(II) [23]. In Figure 1b, an increase in SPC dosage leads to an initial decrease followed by an increase in CST. This observation may be attributed to the excessive addition of oxidants, resulting in smaller sludge flocs and increased release of EPS substances. Moreover, the release of sodium carbonate from SPC may inefficiently consume ·OH according to Equation (5) [6,24]:

$$\cdot OH^- + CO_3^{2-} \rightarrow \cdot CO_3^- + OH^- \quad (5)$$

The contour plot in Figure 1c exhibits the highest degree of ellipticity, indicating that Fe(II) dosage has the most significant interaction with SPC dosage. Additionally, as presented in Table 1, only the p-value of the interaction terms X_1X_2 is <0.05, indicating a significant impact on their interaction.

The 3D response surfaces of the W_c model in this study are presented in Figure 2. Figure 2a,b demonstrate the weak synergistic effects of Fe(II) dosage and initial pH as well as SPC dosage and initial pH. It should be noted that the pH range of 2 to 4 has a minimal impact on the Fenton process and the dissociation of Fe(II) and SPC. Previous studies have reported a wider range of interaction between initial pH and reagents. Moreover, an alkaline condition is unfavorable for the disintegration of SPC, resulting in a low release rate of H_2O_2 [25]. When the initial pH exceeds 4, the precipitation of Fe(III) hinders the

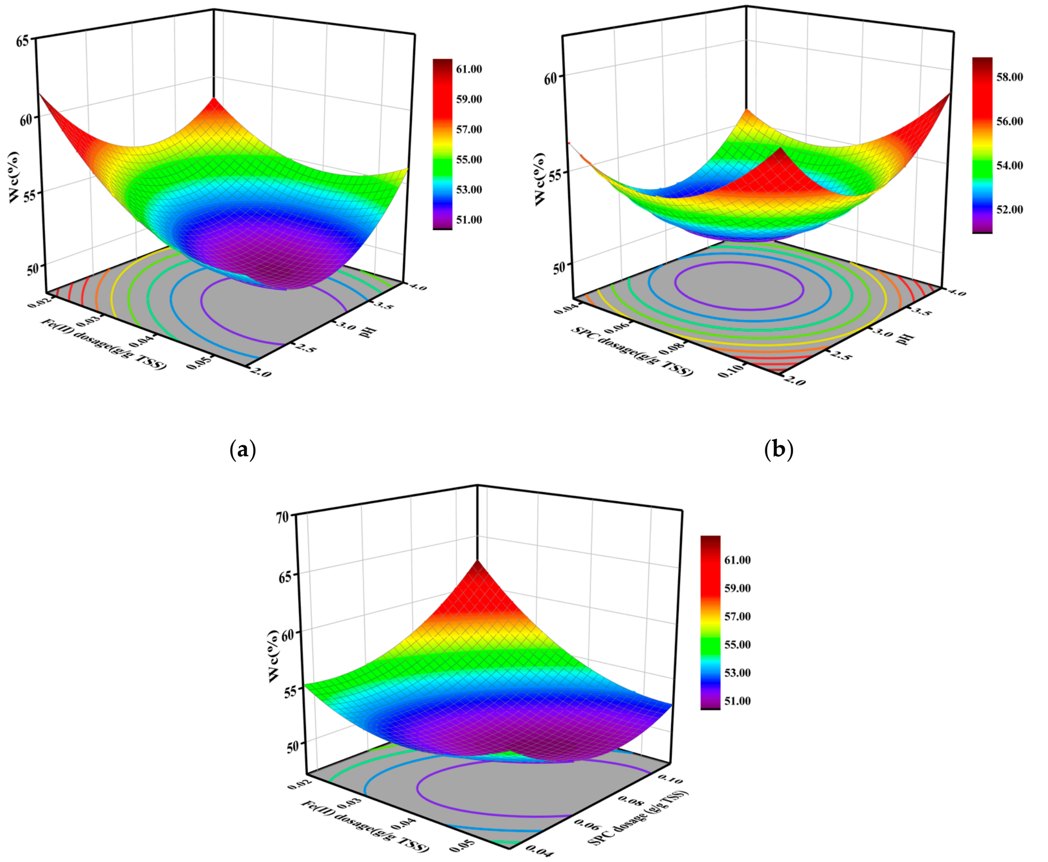
Fe(III)/Fe(II) cycle and the formation of Fe(II) [26,27]. Notably, when the initial pH is set at 3, a minimal water content is achieved with an appropriate dosage of Fe(II) and SPC. Similar to the CST model, Figure 2c demonstrates a strong synergistic effect between Fe(II) dosage and SPC dosage for W_c. Deviating from the optimal dosage of Fe(II) or SPC, whether in excess or in low doses, leads to a decrease in the solids content of the sludge cake. Therefore, from a statistical perspective, proper control of the proportion of these two reagents can further enhance dewatering effects and reduce reagent dosage.



(**a**) (**b**) (**c**)

Figure 1. Response surface diagram for the interaction effect of (**a**) Fe(II) dosage and initial pH; (**b**) SPC dosage and initial pH for CST; (**c**) Fe(II) dosage and SPC dosage for CST.

To optimize the minimum values of CST for conditioned sludge and W_c of the dewatered sludge cake, Design Expert 13 software was employed based on the aforementioned experiments. Table 5 presents the optimal conditions obtained from prediction optimization, which include Fe(II) dosage of 0.05 g/g TSS, SPC dosage of 0.07 g/g TSS, and initial pH of 3.02. Under these conditions, the CST of the conditioned sludge was 30.47 s, and the W_c of the dewatered sludge cake was 50.46%. To validate the reliability of the optimized parameters, three sludge conditioning and dewatering tests were conducted on a full scale under the specified conditions. As shown in Table 6, the CST results were 31.6, 34.1, and 33.5 s, while the W_c results were 51.47, 52.37, and 51.66%. These results were in good agreement with the model predictions, indicating the successful integration of the RSM model and the reliability of the optimal predictions for practical application.



(**a**) (**b**)

(**c**)

Figure 2. Response surface diagram for the interaction effect of (**a**) Fe(II) dosage and initial pH; (**b**) SPC dosage and initial pH; (**c**) Fe(II) dosage and SPC dosage for W_c of dewatered sludge cake.

Table 5. RSM optimal conditions.

Variable	Goal	Upper Limit	Lower Limit	Importance
Fe(II) dosage (g/g TSS)	In range	0.055	0.018	3
SPC dosage (g/g TSS)	In range	0.110	0.036	3
Initial pH	In range	4	2	3
Sludge CST (s)	Minimum	-	-	5
Dewatered sludge W_c (%)	Minimum	-	-	5

Table 6. Verification experiment of sludge dewatering in optimal conditions.

Fe(II) Dosage (g/g TSS)	SPC Dosage (g/g TSS)	Initial pH	Sludge CST (s)		Dewatered Sludge W_c (%)	
			Actual	Predicted	Actual	Predicted
0.05	0.07	3.02	31.6	30.47	51.47	50.46
			34.1		52.37	
			33.5		51.66	

3.2. Effects of Fe(II)/SPC Process on Sludge Structure

In the Fe(II)/SPC system, the disassociation of H_2O_2 and Na_2CO_3 from SPC occurs after mixing with the liquid (Equation (6)). Consequently, Fe(II) promotes the generation of a large amount of highly reactive ·OH (Equation (7)), which facilitates the disintegration of sludge flocs.

$$Na_2CO_3 \bullet 1.5H_2O_2 \rightarrow Na_2CO_3 + 1.5H_2O_2 \quad (6)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + \bullet OH \quad (7)$$

The dewaterability of sludge flocs is closely related to the integrity of cells and the chemical composition of EPS [6,28]. Figure 3 depicts the changes in organic species within the EPS structure. EPS is present as a double-layered structure surrounding the cells, known as LB-EPS and TB-EPS. The retiform nature of EPS impedes sludge floc dewatering by absorbing moisture [8]. Upon treatment with Fe(II)/SPC, the polysaccharide concentration of TB-EPS decreased from 156 mg/L in raw sludge to 127 mg/L in Fe(II)/SPC-conditioned sludge. Conversely, the polysaccharide concentrations of S-EPS and LB-EPS increased from 8.71 mg/L and 34.2 mg/L in raw sludge to 48.0 mg/L and 70.4 mg/L in Fe(II)/SPC-conditioned sludge, respectively. In the case of protein concentrations, LB-EPS and TB-EPS in raw sludge were 2.60 mg/L and 17.6 mg/L, respectively, which reduced to 0.02 mg/L and 4.05 mg/L in the Fe(II)/SPC-conditioned sludge. Consequently, it can be inferred that the macromolecular compounds within the sludge flocs disintegrated and were released into the outer sphere structure.

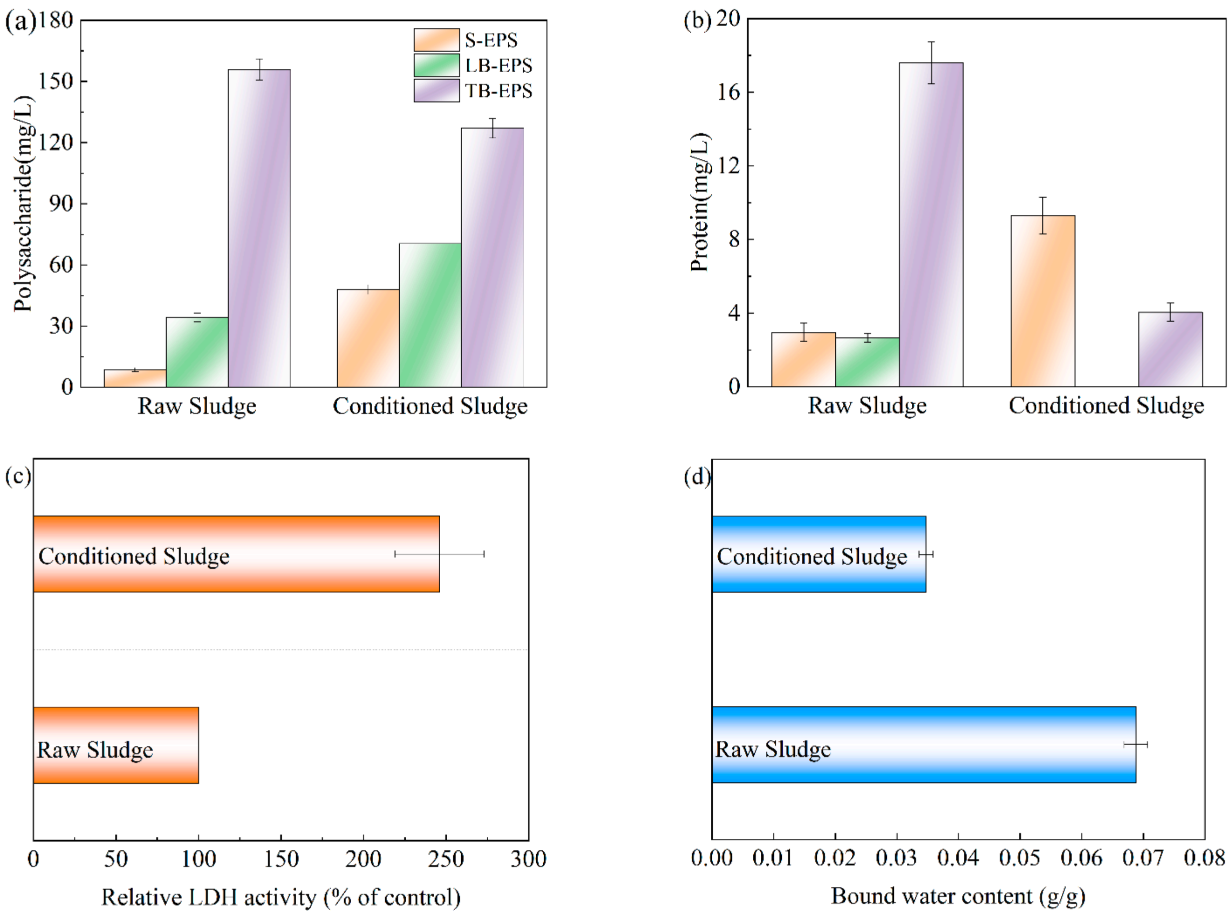


Figure 3. The properties of sludge before and after conditioning: (**a**) polysaccharides and (**b**) protein in EPS layers; (**c**) relative LDH release of the conditioned sludge (raw sludge as the control); (**d**) bound water content.

The release of intracellular water can be used as an indicator of cell integrity in sludge flocs, as determined by the LDH release assay (Figure 3c). LDH is a stable cytosolic enzyme, and an elevation in extracellular LDH levels signifies significant damage to the cell membrane [14]. The LDH activity in the Fe(II)/SPC-conditioned sludge sample was found to be 2.46 times higher than that of raw sludge. This indicates that the Fe(II)/SPC treatment not only degrades EPS but also impairs the integrity of microbial cells, resulting in the release of intracellular water. This finding is supported by the analysis of bound water content.

Bound water refers to water that is tightly bonded to the solid phase through chemical or physical mechanisms within capillary porous bodies [2]. The removal of bound water presents a challenge in sludge dewatering, and a decrease in bound water content is typically caused by the destruction of cell walls or EPS within sludge flocs. The Fe(II)/SPC treatment reduced the bound water content from 0.069 g/g-TSS to 0.035 g/g-TSS, which represents approximately half of the bound water content in the raw sludge.

In summary, the Fe(II)/SPC system generates reactive oxygen species (ROS) that attack sludge flocs, resulting in the breakdown of EPS components (especially proteins) and damage to microbial cells. This leads to modifications in EPS properties and cell status, as well as the disintegration and release of inner sphere macromolecular compounds from sludge flocs into the outer sphere structure, ultimately enhancing sludge dewaterability.

3.3. Practical Implication

For the economic evaluation of this technology, a comparison was conducted between the optimal Fe(II)/SPC technique and other conditioning methods employed at the wastewater treatment plant in Shanwei (Table 7). This plant used to utilize polymeric ferric sulfate (PFS) (1600 USD$/t) to condition sludge. PFS, a commonly employed flocculant, aggregates sludge flocs into larger particles through charge neutralization and adsorption bridging. This effectively prevents the clogging of filter media and the cake layer during filtration, thereby facilitating water passage [29]. As shown in Table 7, dewatered sludge cake following PFS treatment exhibited a moisture content exceeding 62%. This high moisture content contributes to increased transportation and disposal expenses due to the larger sludge volume.

Table 7. Cost analysis for different conditioning processes.

Process	Chemicals	Dosage (t/t TSS)	Unit Price [1] (USD$/t)	Cost (USD$/t TSS)	Total Cost (USD$/t TSS)	W_c (%)
PFS	Polyferric sulfate	0.03	1600	48	48	>62
Fenton	$FeSO_4{\cdot}7H_2O$	0.26	70	18.2	73.65	48–52
	H_2O_2 (27.5%)	0.164	300	49.2		
	H_2SO_4 (98%)	0.05	125	6.25		
Fe(II)/SPC	$FeSO_4{\cdot}7H_2O$	0.233	70	16.31	61.76	51.8
	$NaCO_3{\cdot}1.5H_2O_2$	0.07	560	39.2		
	H_2SO_4 (98%)	0.05	125	6.25		

Note: [1] The unit price refers to the quotation of the Alibaba online mall.

In pursuit of enhanced dewatering performance, the plant has currently been implementing the traditional Fenton process with previously optimized dosages of $FeSO_4{\cdot}7H_2O$ (70 USD$/t), H_2O_2 (27.5%) (300 USD$/t) and H_2SO_4 (98%) (125 USD$/t). The Fenton process involves the utilization of Fe^{2+} and H_2O_2 to generate oxidative ·OH, a process shown to degrade sludge EPS and enhance the release of bound water, thereby improving sludge dewaterability and producing sludge cake with a moisture content of 48–52%. However, it should be noted that the instability and explosiveness of H_2O_2 present a safety hazard in the plant, rendering it unsuitable for full-scale applications. In this study, H_2O_2 was replaced with SPC, which is significantly safer than its predecessor. The Fe(II)/SPC pretreatment was observed to generate reactive oxygen species (ROS) that target the floc structure of sludge, modify EPS properties and cell status, enhance the hydrophobicity and flocculability of sludge, and promote the release of bound water [7]. The moisture content of the dewatered sludge cake after the Fe(II)/SPC process was found to be 51.8%, which closely aligns with the moisture content achieved by the Fenton process (48–52%).

In terms of economic analysis, PFS has the lowest cost of $48 per ton of TSS, but it results in a high moisture content of the sludge cake. Although the traditional Fenton process and Fe(II)/SPC process achieve similar sludge dewatering performances in wastewater treatment, the cost of the Fenton process is $73.65 per ton of TSS, which is much higher than the Fe(II)/SPC process ($61.76 per ton of TSS). Moreover, the traditional Fenton reagents pose safety hazards during transportation and storage, making the Fenton process unsuitable as the primary dewatering technology in wastewater treatment plants. In contrast, the Fe(II)/SPC pretreatment offers a safer alternative, as SPC is less hazardous compared to H_2O_2. This aspect not only ensures the safety of workers but also reduces the costs associated with safety measures and potential accidents.

Considering the cost savings and the safety advantages, the Fe(II)/SPC method presents itself as a promising alternative for sludge conditioning in wastewater treatment plants. It achieves comparable dewatering performance to the traditional Fenton process while offering a cost advantage of $11.89 per ton of TSS due to the lower price of SPC compared to H_2O_2 (27.5%). Moreover, the Fe(II)/SPC method improves the overall sustainability of the wastewater treatment process by reducing transportation and disposal costs and minimizing safety hazards. Therefore, it can be concluded that the Fe(II)/SPC method is a cost-effective and environmentally friendly option for sludge conditioning in wastewater treatment.

4. Conclusions

In this study, a full-scale application of the Fe(II)/SPC sludge conditioning process was conducted. An RSM-based prediction model was established to determine the moisture content and CST under the Fe(II)/SPC process. The regression equations for CST and W_c had high R^2 values of 0.9524 and 0.9307, respectively, indicating a good fit. The optimal parameters determined through RSM were an initial pH of 3.02, Fe(II) dosage of 0.05 g/g TSS, and SPC dosage of 0.07 g/g TSS. The validation test confirmed the accuracy of the prediction results, with the conditioned sludge exhibiting a CST of 31.6 s and a moisture content of 51.47%. Furthermore, when compared to PFS and Fenton processes, the Fe(II)/SPC process demonstrated higher economic efficiency and safety, while maintaining good dewatering performance. Overall, the Fe(II)/SPC treatment shows promise as a prospective sludge dewatering and conditioning process.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15213838/s1, Table S1: Characteristics of the raw sludge. Figure S1: Full-scale equipment for sludge conditioning and dewatering: (a) Reagent tank, (b) sludge conditioning tank, (c) high-pressure plate–frame diaphragm filter, (d) dewatered sludge collection system.

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