

# Response Surface Methodology for the Optimization of Zn-Contaminated Soil Remediation by Soil Washing with Water-Soluble Chitosan

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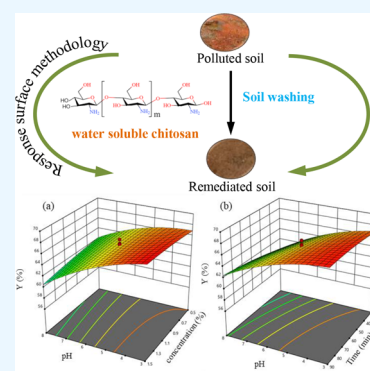
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**ABSTRACT:** Soil washing is an important method for the remediation of contaminated soil. This research presents the optimization of soil washing conditions in the remediation of Zn-contaminated soils with water-soluble chitosan (WSCS). Response surface methodology (RSM) was used to optimized the washing conditions after single factor experiments. The central composite design (CCD) with three factors and five levels was applied to the optimization of the removal efficiency of Zn from soils, and WSCS concentration, pH value, and washing time were evaluated variables in the washing process. Results indicated that the pH value ( $p < 0.0001$ ) was the most significant factor which mainly affected the distribution and content of metal species in aqueous solution, ion exchange and adsorption/desorption behavior of metals, solubility of chelating agent, as well as readsorption of metal complexes. The optimal conditions for the Zn removal from soils were WSCS concentration of 1.5%, pH of 3.3, and washing time of 72 min. The removal efficiency could reach 65.4% under the optimized conditions, which was close to the predicted value of 68.3% by the response surface method. Therefore, it could be found that the response surface methodology was an effective method to determine the optimal conditions for the removal of metals from contaminated soils by soil washing.



## 1. INTRODUCTION

Soil heavy metal pollution has become a global concern because of the high toxicity to the ecosystem and human health. “National Soil pollution situation investigation bulletin” released by the Ministry of Environmental Protection and the Ministry of Land and Resources of China indicated that the soil pollution by potentially toxic metals (PTMs) is serious throughout the country in China. Soil washing is one of the most widely and studied off-site techniques for remediation of soils highly contaminated with PTMs.<sup>1–4</sup> Soil washing is a method in which a system uses a chemical solution to wash the surface and pores of polluted soils through dissolution or desorption action, leading to the fact that PTMs could be transferred from the soil to the solution so as to achieve the purpose of remediation of contaminated soil.<sup>5</sup> Soil washing is often used for soil remediation due to the rapid and highly efficient removal of PTMs from contaminated soils, reduction or elimination of long-term potential ecological threats, and high cost-effectiveness. Soil remediation by soil washing is influenced by a number of factors, including the type and nature of the soil, the concentration and solubility of PTMs, and the type of washing agent. Various washing agents have been studied and applied in soil remediation, such as inorganic acids, organic acids, surfactants, and chelating agents. Nevertheless, although some agents are effective in the removal of PTMs from soils, there are some problems such as changes of

basic properties for soils and the toxicity and nonbiodegradability of the washing agents.

At present, many researchers are increasingly concerned about the natural chelating agents as the new kind of washing agents due to the high binding capacity with metal ions. Chitosan is the second most abundant naturally available polymer and is a natural chelating agent of heavy metals.<sup>6</sup> Particularly, chitosan has the advantages of low price, abundant resources, antibacterial character, nontoxicity, biocompatibility, biodegradability, macromolecular structure, hydrophilicity, cationic nature, active sites, strong adsorption capacity, and so on. Currently, chitosan-based environmental materials have been widely and successfully applied in the field of water treatment.<sup>6–8</sup> Nonetheless, chitosan as the washing agent has rarely been studied in soil remediation due to its poor water-solubility in a  $\text{pH} \geq 7$  solution.

Experimental design as a valuable mathematical technique is applied to statistical modeling and systematic analysis.<sup>9,10</sup> Response surface methodology (RSM) is a statistical

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experimental design that can be used for process development, optimization of product design and formulation, and performance.<sup>11</sup> RSM can effectively optimize parameters and significantly reduce the numbers of experiments required to predict optimal conditions.<sup>12</sup> The central composite design (CCD) is a standard, effective, and most commonly used design of RSM. With a reasonable number of design points and reliable curvature estimates, CCD is an ideal method for assigning operational individual variables to an evaluation range in order to obtain a reasonable amount of information for testing lack-of-fit.<sup>13</sup> Gitipour et al.<sup>3</sup> investigated effective parameters in washing of contaminated soils by polycyclic aromatic hydrocarbons (PAHs) using a response surface methodology. He et al.<sup>14</sup> optimized washing conditions for the removal of multiple metals (Cu–Pb–Zn–Cd) by EDTA, and experiments were determined by RSM.

The objective of this study was to investigate and optimize the removal efficiency of Zn from contaminated soils with water-soluble chitosan (WSCS) as the washing agent by a central composite design (CCD). Three variables including pH value, WSCS concentration, and washing time in the washing process were investigated in order to optimize the independent variables and obtain the optimal conditions.

## 2. EXPERIMENTAL SECTION

**2.1. Soils and Chemicals.** The original soil samples were collected from flower and plant nursery stock bases in Guilin city of China. The soils were air-dried and ground to a 1 mm sieve, then homogenized and stored until analysis. Table 1

**Table 1. Physicochemical Characteristics of the Original Soils**

soil properties	value	method
pH	6.52	HJ962-2018
organic matter (g·kg <sup>-1</sup> )	22.49	NY/T 1121.6-2006
CEC (cmol kg <sup>-1</sup> )	19.36	HJ 889-2017

summarized the main characteristics of the soils and the respective measurement methods. All chemicals used in the experiments were purchased at the analytical purity. Zinc nitrate hexahydrate was bought from Xilong Scientific Co., Ltd., Guangzhou, China. Water-soluble chitosan (WSCS) was obtained from Shandong Weikang Biomedical Technology Co. Ltd., Linyi, China. The ammonium acetate was from Guangdong Guanghua Sci-Tech Co., Ltd., Shantou, China.

**2.2. Contaminated Soils.** An amount of 6.9 g of zinc nitrate hexahydrate was added to 1.0 kg soil samples. The contaminated soils were placed for 1 month with intermittent wetting and stirring. Finally, the contaminated soils were air-dried, ground over 100 mesh sieve, and placed in the airtight bags for the later use. The content of Zn was determined by flame atomic absorption spectrophotometer (AAS, TAS-990, Beijing General Instrument Co., Ltd., China). The total Zn content of the contaminated soils was 1436.04 g kg<sup>-1</sup> determined by the HNO<sub>3</sub>/HF/HClO<sub>4</sub> digestion method.

**2.3. Single-Factor Experiments.** A series of single factor experiments were conducted to determine the preliminary ranges of conditional variables such as solution pH value, WSCS concentration, and washing time with a liquid-to-soil ratio of 25:1 (v/w) in 50 mL plastic centrifuge tubes. For each run, 1.0 g of contaminated soil was placed in a series of 50 mL plastic centrifuge tubes. Each treatment was repeated three

times, and the pH value of the solution was adjusted to 5.0 with 0.1 mol L<sup>-1</sup> HCl or NaOH. To investigate the effects of pH value on the removal of metals in the soil, the tests were based on 1.0% washing solution at a range of pH values from 3.0 to 8.0. The WSCS concentrations were set as 0, 0.2, 0.4, 0.6, 0.8, and 1%, respectively. The solution was oscillated at 25 °C for 2 h, then centrifuged at 5000 rpm for 10 min, and filtered through a filter membrane (0.45 μm). The concentrations of Zn ions in the solution were determined by flame atomic absorption spectrometry. The removal efficiency of Zn was calculated by eq 1.

$$\text{removal efficiency (\%)} = \frac{C_L V_L}{C_0 M} \times 100\% \quad (1)$$

where  $C_0$  (mg kg<sup>-1</sup>) and  $C_L$  (mg L<sup>-1</sup>) are the content of Zn in the original contaminated soil and in the supernatant after washing, respectively,  $V_L$  (L) is the supernatant liquid volume, and  $M$  (kg) is the mass of the soil.

**2.4. Response Surface Methodology Design.** The RSM design procedure usually contained the following four stages: first, a series of experiments designed to fully and reliably determine the desired target response; second, the second-order mathematical response model obtained by the optimal fitting method; third, the establishment of the optimal parameters for the research variables corresponding to the maximum or minimum response value; finally, the analysis and representation of synergistic effects of process parameters with two- and three-dimensional (3D) plots.

An independent variable center composite design (CCD) based on RSM was used to establish the optimal synergistic effect and check the response pattern.<sup>15,16</sup> According to the preliminary experiments, the specific parameters were pH ( $X_1$ ), WSCS concentration ( $X_2$ ), and washing time ( $X_3$ ). CCD involved  $2^n$  factorial runs,  $2n$  axial runs, and  $n_c$  center runs. The total experimental runs ( $N$ ) were calculated by eq 2.<sup>12</sup>

$$N = 2^n + 2n + n_c \quad (2)$$

where  $n$  is the number of independent variables and  $n_c$  is the number of center points, the value of which could be set between 2 and 6. In addition, the independent variables in CCD were coded in five levels of  $(-\alpha, -1, 0, +1, +\alpha)$  as illustrated in Table 2. In this study, experiments with 20 runs

**Table 2. Independent Variables for the Soil Washing with the Actual and Coded Levels**

variables	code	variable levels				
		lowest, $-\alpha$	low, $-1$	center, 0	high, 1	highest, $+\alpha$
pH	$X_1$	1.3	3	5.5	8	9.7
WSCS concentration (%)	$X_2$	0.16	0.5	1	1.5	1.84
washing time (min)	$X_3$	9.5	30	60	90	110

were conducted with eight cubic points (coded as  $\pm 1$ ), six axial points (coded as  $\pm \alpha$ ), and six replication of center points (coded as 0) for the modeling and optimization process.

The influence of individual variables from experiments were analyzed by the software Design Expert 12.0, and the data were fitted for the regression analysis in order to optimize the variables in the washing experiments. The evaluation of

statistical significance and quality of the model was obtained by an analysis of variance (ANOVA) test. The performance of the response surface was analyzed with the regression polynomial equation. The regression coefficients of linear, quadratic, and interaction terms could be obtained by ANOVA analysis. The most frequently applied mathematical models were tested by linear, two factorial interaction (2FI), quadratic, and cubic functions. Four models could be respectively expressed as the following equations:<sup>10,11</sup>

linear

$$Y = \beta_0 + \sum_{i=1}^m \beta_i X_i + \varepsilon \quad (3)$$

2Fi

$$Y = \beta_0 + \sum_{i=1}^m \beta_i X_i + \sum_{i<j=2}^m \beta_{ij} X_i X_j + \varepsilon \quad (4)$$

quadratic

$$Y = \beta_0 + \sum_{i=1}^m \beta_i X_i + \sum_{i=1}^m \beta_{ii} X_{ii}^2 + \sum_{i<j=2}^m \sum_{i=1}^m \beta_{ij} X_i X_j \quad (5)$$

cubic

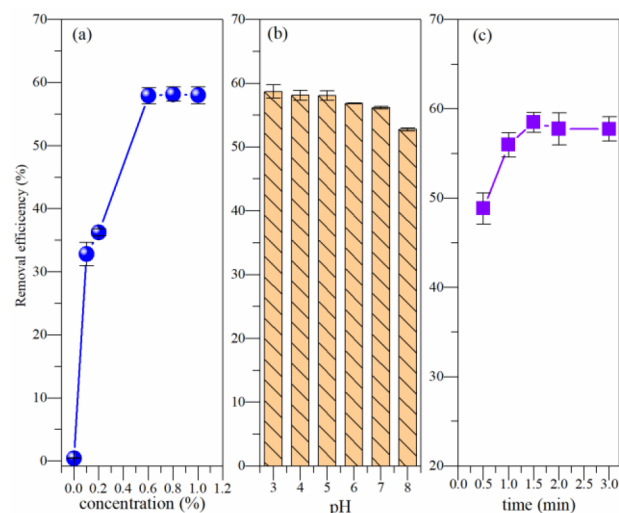
$$Y = \beta_0 + \sum_{i=1}^m \beta_i X_i + \sum_{i=1}^m \beta_{ii} X_{ii}^2 + \sum_{i<j=2}^m \sum_{i=1}^m \beta_{ij} X_i X_j + \sum_{i<j<k=3}^m \sum_{i=1}^m \beta_{ijk} X_i X_j X_k \quad (6)$$

where  $Y$  represents the variable of response,  $X_i$ ,  $X_j$ , and  $X_k$  are the coded values of independent variables,  $\beta_0$  is the constant,  $\beta_i$  is the linear coefficient, and  $\beta_{ii}$ ,  $\beta_{ij}$ , and  $\beta_{ijk}$  represent the quadratic and interaction coefficients, respectively. Random error ( $\varepsilon$ ) indicates the measure of difference between observed and predicted values.

### 3. RESULTS AND DISCUSSION

**3.1. Single-Factor Experiments.** The effects of WSCS concentration, pH value, and washing time on the removal of Zn from soils were investigated in the preliminary experiment. Figure 1a illustrates the effects of WSCS concentration on the removal of Zn from soils when the pH value was 6.0 and the washing time was 120 min. The significance of washing with deionized water was to provide information on metal components that were weakly bound to soil particles. The remaining fractions of the metals were thought to be strongly bound and immobilized within the soil matrix under natural-water conditions.<sup>17</sup> It can be observed that the removal efficiency increased sharply from 0.4% to 56.9% with increasing WSCS concentration from 0 to 0.6%. A higher concentration of chelating agent could bind more heavy metal ions and promote the chelating reaction to move toward the direction to the formation of chelating compounds. To further improve the concentration of chitosan solution did not enhance the removal efficiency of Zn from the soils, indicating that the residual Zn in the soils could not be removed by more WSCS.

The effects of pH values on the removal of Zn from soils are given in Figure 1b. The removal efficiency decreased from 58.7% to 52.7% with increasing pH from 3.0 to 8.0. The pH value of the washing solution played an important role in the



**Figure 1.** Effects of WSCS concentration (a), pH values (b), and washing time (c) on removal efficiencies of Zn from soils. The error bars represent the standard deviation of the mean of the three samples.

extraction process of heavy metals from soils, mainly affecting the distribution and content of metal species in aqueous solution, ion exchange behavior, adsorption/desorption processes, solubility of chelating agent, as well as the readorption mechanism associated with newly formed metal complexes.<sup>18</sup> Generally, the acid washing solution could dissolve the heavy metal ions combined with soil colloids, and more hydrogen ions on the soil surface could promote the desorption of metal ions. With the increase of the number of hydrogen ions, the protonation degree on the surface of soil particles became higher and higher, which also promoted the desorption of metal ions. When  $\text{pH} > 7.0$ , metal ions will be gradually converted into metal hydroxyl complexes or metal oxides with low solubility.

The effects of washing time on the removal of Zn from soils are given in Figure 1c. A rapid initial release rate of Zn into the washing solution indicated the dissolution of weakly bound metals adsorbed at easily coordinated locations on the surface of soil particles, or the rapid dissolution of fine sediments. The continued slow release of Zn from soils may be due to the reaction with adsorbed or precipitated metal species that bind more strongly to the internal surface sites.

**3.2. Evaluation of Simulated Run by CCD.** CCD served as a statistical design to determine the relationship between the factors (pH, WSCS concentration, and washing time) and the response ( $R_{\text{Zn}}$ ). The response ( $R_{\text{Zn}}$ ) was evaluated in the 20 experimental runs by CCD, which is summarized in Table 3. The highest removal efficiency of 68.1% was obtained at run number 20 with the conditions of pH 1.3, 1.0% CS concentration, and 60 min washing time. The lowest removal efficiency (57.2%) was obtained under the conditions with pH of 9.7, 1.0% WSCS concentration, and washing time of 60 min.

According to the experimental design matrix for the removal of Zn from contaminated soils, the results were tested by linear, two-factor interaction (2FI), quadratic, and cubic models for all runs in order to obtain the regression equation. Two different tests, namely, the sequential model and lack of fit were conducted to determine the adequacy of various models. The response surface model can be selected as the best model based on the following criteria: the highest order

**Table 3. Experimental Design Matrix for the Removal of Zn from Contaminated Soils**

run	$X_1$ : pH	$X_2$ : WSCS concentration (%)	$X_3$ : washing time (min)	Y (%)	
				measured	predicted
1	9.70	1	60	57.2	57.3
2	5.5	0.16	60	65.0	65.5
3	8	0.5	90	62.8	63.0
4	5.5	1	60	65.0	65.8
5	3	0.5	30	66.0	66.0
6	5.5	1	60	66.0	65.8
7	8	0.5	30	61.5	60.8
8	3	1.5	90	67.6	68.6
9	3	0.5	90	67.3	67.2
10	5.5	1.84	60	66.0	65.2
11	5.5	1	60	65.6	65.8
12	8	1.5	90	61.2	61.5
13	5.5	1	60	66.9	65.8
14	3	1.5	30	67.1	67.1
15	5.5	1	9.5	63.0	63.4
16	5.5	1	60	66.2	65.8
17	8	1.5	30	58.7	59.0
18	5.5	1	60	65.2	65.8
19	5.5	1	110.5	67.2	66.5
20	1.30	1	60	68.1	67.7

polynomial with additional significant terms and the model is not aliased.<sup>19</sup> Based on the regression coefficients (Table 4),

**Table 4. Model Summary Statistics for the Removal of Zn from Contaminated Soils**

source	sequential $p$ -value	lack of fit $p$ -value	adjusted $R^2$	predicted $R^2$	
linear	<0.0001	0.0378	0.7841	0.7084	
2FI	0.5342	0.0298	0.7741	0.5829	
quadratic	0.0013	0.3490	0.9345	0.8206	suggested
cubic	0.2548	0.4689	0.9498	0.5976	aliased

the quadratic model with highest regression values was considered a suitable model to describe the experimental results. Except for the cubic model which was aliased, the

**Table 5. ANOVA Analysis for the Quadratic Model**

source	sum of squares	degree of freedom	mean square	$F$ -value	$p$ -value	comments
model	167.39	9	18.60	31.11	<0.0001	significant
$X_1$	129.98	1	129.98	217.43	<0.0001	
$X_2$	0.13	1	0.13	0.21	0.6544	
$X_3$	11.74	1	11.74	19.64	0.0013	
$X_1X_2$	4.20	1	4.20	7.03	0.0242	
$X_1X_3$	0.50	1	0.50	0.84	0.3819	
$X_2X_3$	0.020	1	0.020	0.033	0.8585	
X2 1	20.21	1	20.21	33.81	0.0002	
X2 2	0.45	1	0.45	0.75	0.4060	
X2 3	1.46	1	1.46	2.44	0.1494	
residuals	5.98	10	0.60			
lack of fit	3.53	5	0.71	1.44	0.3490	not significant
pure effort	2.45	5	0.49			
cor. total	173.37	19				correlation coefficient ( $R^2$ )
adjusted $R^2$		0.9345				coefficient of variation (%)
predicted $R^2$		0.8206				adeq. precision

quadratic model was found to have the maximum adjusted  $R^2$  (0.9345) and predicted  $R^2$  (0.8206). Additionally, for a suitable model, it must have a nonsignificant lack of fit. The lack of fit  $p$ -values for the linear and 2FI models was below 0.05, implying that the lack of fit was significant in relation to the large pure error. The lack-of-fit test was not significant ( $p$ -value > 0.05), so the quadratic model was suitable for representing the experimental data in this research. Consequently, the quadratic model was selected for the further analysis.

The second-order polynomial expression in terms of coded values from the ANOVA is expressed as eq 7 with 10 coefficients.

$$Y = 65.83 - 3.09 \times X_1 - 0.097 \times X_2 + 0.93 \times X_3 - 0.72 \times X_1X_2 + 0.25 \times X_1X_3 + 0.05 \times X_2X_3 - 1.18 \times X_1^2 - 0.18 \times X_2^2 - 0.32 \times X_3^2 \quad (7)$$

The positive signs indicated the synergistic effect of factors, and the negative signs indicated the antagonistic effect of factors in the model. It was evident that pH presented a negative effect on the removal of Zn from soils. The pH value usually affected the oxidation, reduction, precipitation, adsorption, and coordination reactions of metals as well as the speciation and subsequent transformation and migration of heavy metals in soils. In the acidic environment, protons adsorbed to the mineral surface of soils could promote the replacement of metal ions or the dissolution of the mineral crystal lattice of soils. In addition, the pH value also had a great influence on the solubility, speciation, and transformation of the washing agents, and then also significantly affected the removal efficiencies of heavy metals from soils. The increase of washing time was beneficial to the increase of removal efficiency, which could be explained by the slow dissolution kinetics of mineral/organic matter-bound metals from soils.

Analysis of variance (ANOVA) was performed on the experimental results to determine the accuracy and significance of the model, and the results are given in Table 5. As can be seen from Table 5, the correlation coefficient ( $R^2$ ) value was 0.9646, indicating that the model obtained was highly significant and adequate. 96.46% of the data variation could be explained and only 3.54% of the total variations could not

be explained by the model. Generally, the  $R^2$  value of the model should not be less than 0.75 for a suitable model.<sup>20</sup> However, a large  $R^2$  value does not necessarily mean that the regression model is good, and the inference is only true based on the similarly high value of adjusted  $R^2$ .<sup>2,12</sup> In this study, the correlation coefficient ( $R^2 = 0.9655$ ) value was consistent with the adjusted  $R^2$  value (0.9345), indicating that the regression model was significant and fitted well with the experimental data. The difference between the adjusted and predicted values was less than 20%, indicating that the adjusted  $R^2$  was in reasonable agreement with the predicted  $R^2$  (0.8206).<sup>21,22</sup>

Furthermore, the significance of linear, interaction and quadratic model terms were determined using the analysis of variance (ANOVA) as presented in Table 5. The Fisher variation ratio ( $F$ -value), probability of error value ( $p$ -value), lack of fit and adequate precision were all evidence of ANOVA. Generally, the  $p$ -value (probability of error value) less than 0.05 suggested that terms of the model were significant.<sup>11,23</sup> The high  $F$ -value of 31.11 and the  $p$ -value below 0.0001 implied that the model was significant and adequate in the washing process.<sup>24</sup> Moreover, the small value of coefficient of variation (CV, %) suggested that the acceptable variation and reproducibility of the model for the further prediction of Zn removal within the range of research variables.<sup>19,25</sup> Additionally, it was desirable that an appropriate regression model had a greater adequate precision ( $>4.0$ ), which was used for representing the signal-to-noise ratio.<sup>26</sup> In this study, the quadratic model had an adequate precision with a high ratio of 20.67. Therefore, it was concluded that this model could be used to navigate the design.

Additionally, it could be observed from Table 5 that pH ( $X_1$ ), washing time ( $X_3$ ), the interaction term of  $X_1X_2$  and the quadratic term of  $X_2^2$  were significant terms in the model, whereas other terms were negligible relative to the removal of Zn from soils. The most significant variable influencing the removal efficiency was the linear term of ( $X_1$ ), indicating that the pH value ( $p < 0.0001$ ) was the most significant factor. Similarly,  $X_3$ ,  $X_1X_2$  and  $X_2^2$  were the significant terms with a  $p$ -value of less than 0.05 for the Zn removal by soil washing.

In order to verify the effectiveness of the prediction model, Figure 2 presents the comparison plot of the predicted against experimental values for the removal of Zn from soils. As can be

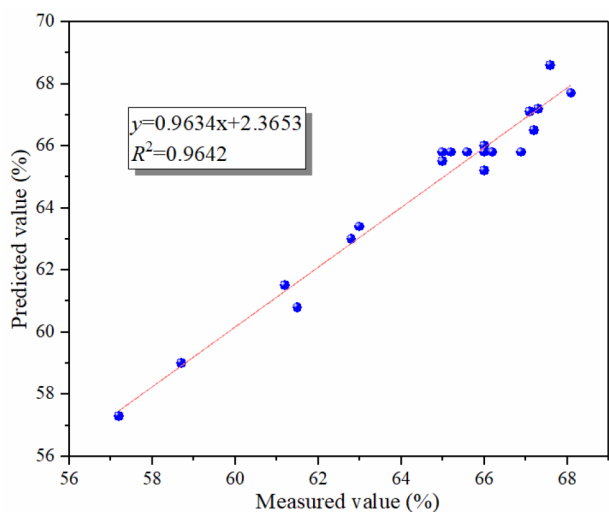
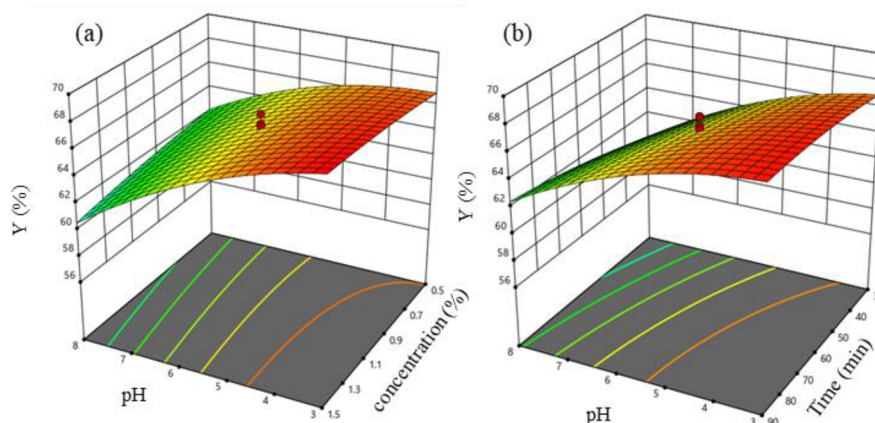


Figure 2. Plot for predicted vs experimental values.

seen from the diagram, most of the actual values were uniformly and closely distributed to the predicted values, and data points were almost divided equally by the 45° line. Results indicated that the experimental data had a reasonable agreement with the predicted response values ( $R^2 = 0.9642$ ). As a consequence, the regression model can effectively describe the relationship between various factors and responses within the research range. Because the data points were uniformly distributed near or on a straight line, the error within the operating parameter boundary could be ignored. In other words, the regression equation fitted well with the experimental data, which further verified the accuracy and application of the second-order model for the removal of Zn from soils by soil washing with WCS.

Figure 3 displays a three-dimensional (3D) response surface diagram of the interaction effects of independent variables on the removal efficiency ( $Y$ ) of Zn from soils. For 3D surface diagrams, two variables were changed while the third variable remained constant at the zero coded level. The 3D graphs could provide support for illustrating more information about the behavior of the system and could describe the level and nature of interactions of independent variables as a function of factors on the removal efficiency of Zn from soils.<sup>27,28</sup> The interactions among factors could be described by the shape of contour lines, and the elliptic contour lines indicated a significant interaction, while the circular contour lines indicated an insignificant interaction between corresponding variables. The trends of removal efficiency of Zn from soils against varying pH values and WCS concentration are illustrated in Figure 3a, where the washing time was fixed at the zero level (60 min). The change in color of the plot from green to yellow and red indicated low, middle, and high value of removal efficiency of Zn from soils. It could be found that the removal efficiency was strongly associated with the pH value and WCS concentration, and the maximum removal efficiency was at pH 3.0 and WCS concentration of 1.5%. This may be explained by the fact that the high concentration of washing agent could combine with more Zn ions and the complexation reaction between Zn ions and ligands to move toward the direction of chelate formation. Nevertheless, the varying level of WCS concentration was not particularly critical in the removal of Zn from soils. Protonation of functional groups in soil colloids at lower pH values facilitated desorption of heavy metals from the soil surface. In addition, hydrogen ions were weak competitive cations, which could replace the zinc absorbed in the soils through cation exchange, thus leading to the removal of Zn from soil. The removal efficiency of Zn changed little with the increasing concentration of WCS from 0.5% to 1.5% at neutral pH. As  $pH > 7$  in the solution, the removal efficiency of Zn slightly decreased with the increase of WCS concentration from 0.5% to 1.5%. Under the condition of higher pH, the viscosity of the washing solution increased with the increasing concentration of WCS. The emulsion became relatively stationary and highly viscous, preventing the washing agent from penetrating the interface between the soil and the metal, which was not conducive to the washing of Zn from soils. Accordingly, the higher pH value had an antagonistic effect on the removal of Zn from soils. Similar trends were also observed by Wang et al.<sup>29</sup> and Yang et al.<sup>30</sup>

Figure 3b represents the effects of pH and washing time on the removal efficiency of Zn from soils, where the WCS concentration was fixed at the zero level (1%). The 3D model illustrated an increase in pH from 3.0 to 8.0 and washing time



**Figure 3.** 3D plots of removal efficiency of Zn as a function of the interaction between factors: (a) pH vs WSCS concentration and (b) pH vs washing time when other variations were at center points.

from 30 to 90 min. It could be found that the removal efficiency was strongly associated with the pH value and washing time, and the maximum removal efficiency was at pH 3.0 and washing time of 90 min. The lower pH was conducive to the release of more metals with the same washing time, and the increasing washing time was beneficial to the release of more metals with the same pH value. In other words, the lower pH was beneficial to improve the removal efficiency of Zn from soils. More hydrogen ions competed with metal ions in the washing system with the decrease of solution pH, which promoted the dissolution of zinc compounds, resulting in a decrease in the cationic heavy metals adsorbed on the soils and an increase of removal efficiency of Zn from soils. The similar phenomenon and results have been discussed when soil washing is used to remove heavy metals from contaminated soil.<sup>30,31</sup> Nevertheless, the effect of washing time did not seem to be significant. Similarly, some studies had shown that the removal of contaminants from soils depended on the concentration of the washing agents, not the washing time.<sup>32,33</sup> In this study, there was a weak effect on the removal efficiency between WSCS concentration and washing time at the zero level (pH = 5.5), and the 3D plots were not shown.

**3.3. Optimization of Washing Conditions.** One of the main objectives of this study was to obtain the optimal washing conditions for remediation of Zn-contaminated soils with chitosan as the washing agent. The response surface regression equation was used to optimize three parameters including pH, WSCS concentration, and washing time to obtain the highest removal efficiency of Zn from soils (Table 6). The optimal removal efficiency of 68.3% was obtained from the second-order polynomial equation at pH 3.3, 1.5% WSCS, and washing time of 72 min. In order to verify the applicability of the model, three validation experiments were carried out under

**Table 6.** Optimal Independent Variables and Predicted Maximum Removal Efficiency

pH	WSCS concentration (%)	washing time (min)	removal efficiency (%)	
			measured	predicted
3.3	1.5	72	65.4	68.3
8.0	1.5	30	58.7	59.0
8.0	1.5	90	61.2	61.5

the optimal washing conditions. The removal efficiency of 65.4% was in good agreement with the predicted value ( $p < 0.05$ ), which proved that the RSM model was suitable for optimizing the removal of Zn from soils. It is worth noting that the removal efficiency remained at a relatively high level when the WSCS solution was at a higher pH value. Although the efficiency decreased with increasing pH, it was higher than 50% at a pH value of 8.0 (seen in Table 3). Therefore, it could be considered that water-soluble chitosan broadened the application range of original chitosan.

#### 4. CONCLUSION

It is very important to select and determine the effective parameters during the washing process and remediation of contaminated soil. A mathematical model was established to determine the influence of influencing parameters on the soil washing process by a response surface experiment design method. The quadratic model equation was established, and the removal efficiency of Zn from soils was expressed as a function of the independent variables pH, WSCS concentration, and washing time. Analysis of variance revealed that pH, chitosan concentration, and interactions had significant effects on the removal efficiency of Zn from soils. Moreover, the experimental values were close to the predicted values, which confirmed the adequacy of the model. All results indicated that the CCD was a reliable tool for the optimization of experimental conditions for soil remediation by soil washing.

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## Notes

The authors declare no competing financial interest.

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